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JURATE VIRKUTYTE

Heavy Metal Bonding and Remediation Conditions in Electrokinetically Treated Waste Medias

Doctoral dissertation

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Department of Applied Physics

Author´s address:
University of Kuopio
Department of Environmental Sciences
Laboratory of Applied Environmental Chemistry
P.O. Box 181
FIN-50101 MIKKELI
FINLAND
Tel. +358 15 355 6201
Fax +358 15 355 6365
E-mail: jurate.virkutyte@uku.fi

Supervisors:
Professor Mika Sillanpää, Ph.D.
University of Kuopio

Dr. Ir. Piet N. L. Lens, Ph.D.
University of Wageningen
Wageningen, The Netherlands

Reviewers:
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Opponent:
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ABSTRACT

The main aim of the doctoral thesis was to examine the electrokinetic remediation of sand, timber waste and anaerobic granular sludge, with particular reference to the influence of electrode number and spacing, electrokinetic cell layout, contaminants placement in the cell, pH, electric current, chelating agents, drainage and matrix aging on the basis of improving the contaminants desorption processes. The effect of contaminant bonding in different waste media on the electrokinetic remediation process was also evaluated. The aims were researched through laboratory scale experiments and computer based modeling.

Theoretical considerations in first two chapters assisted in the design of an 'open' electrokinetic laboratory scale device used throughout the doctoral research.

The sand was chosen as a sample porous medium to examine its feasibility for electrokinetic remediation as an alternative to conventional techniques. CCA-treated timber waste may pose a significant threat to the environment, if leaching of dangerous chemicals occurs during landfilling. The disposal of contaminated sludge from pulp and paper industry is a constantly growing problem in Finland. Therefore it is a good practice to assess the applicability of those matrices to be treated by electrokinetic method.

The thesis showed for the first time that electrokinetic technology is applicable for all three selected matrices, especially the sand. Results, presented in Chapter 3, have proved that electrokinetic remediation is a successful alternative to pump and treat technologies as copper and chromium removal efficiencies from sand as high as 91% can be attained. Addition of oxalic acid or EDTA induced the solubilization of copper and chromium from CCA-treated timber waste (Chapter 4). However, the addition of chelating agents was not efficient in solubilizing copper from anaerobic granular sludge granules (Chapter 6).

As discovered in Chapter 5 and 6, the fractionation and migration of heavy metals and copper in particular, within the granular sludge matrix was found to be highly dependent on the experimental conditions, i.e. pH, complexation and layout of the electrokinetic cell. The 'open' cell layout yielded higher copper and iron transport under the applied electric field than the 'closed' cell, therefore 'open' cell layout may be more efficiently applied *in situ*.

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CAB Thesaurus: environmental protection; waste treatment; industrial wastes; electrical treatment; pollutants; contaminants; heavy metals; copper; chromium; sand; soil pollution; waste wood; paper mill sludge

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Jūratė Virkutytė
Mikkeli, Finland, 2005.

ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
AN	Anion-exchange membrane: membrane containing fixed cationic charges and mobile anions that can be exchanged with other anions present in an external fluid in contact with the membrane
AQDS	9, 10-anthraquinone-2, 6-disulfonic acid
AQS	Anthraquinone-2-sulfonate
Bulk density	Oven dry soil weight (g) / Volume of soil solids and pores
C	Concentration of any compound (in $mg.kg^{-1}$ or $mg.l^{-1}$)
C_o	Initial concentration of any compound (in $mg.kg^{-1}$ or $mg.l^{-1}$)
CAT	Cation-exchange membrane: membrane containing fixed anionic charges and mobile cations which can be exchanged with other cations present in an external fluid in contact with the membrane
CAR	Contaminant accumulation rate
COD	Chemical Oxygen Demand (in mg O_2 l^{-1}): amount of oxygen needed to completely oxidize all solutes present
CCA	Chromated copper arsenate
CEC	Cation exchage capacity (in $meg.100g^{-1}$)
CEC	Council of the European Communities
Current density	Determines the deviation of the electrode potential from its equilibrium value when an external current is passed
DC	Direct current
E	Oxidation potential (V and reference electrode potential)
EDTA	Ethylene diamine tetraacetic acid
EEC	European Economic Commission
Eh	Redox potential
Electrodialysis	Membrane-based separation process in which ions are driven through an ion-selective membrane under the influence of an electric field
Electromigration	Movement of ionic species in the media-water solution
Electroosmosis	Bulk flow of moisture present in the contaminated media from the anode to the cathode
Electrophoresis	Movement of charged particles or colloids in the applied electric field
EPS	Exocellular polymeric substance
I	Electric current (in A)
ICP – OES	Inductively Coupled Plasma Optical Emission Spectrophotometer
Ion	Species will positive or negative charges
Limiting current density	Current density at which dramatic increases in resistance are observed in an ion exchange membrane system under the influence of an applied electric field between the upstream and downstream
M	Moles per liter
Membrane	Structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces
NMR	Nuclear Magnetic resonance imaging
Polarization of electrodes	Change in potential of both electrodes involved in the electrolysis process
t	Electrokinetic treatment time (in h)
E	Electric field strength (in $V\ m^{-1}$)
V	Applied voltage (in V)
r	Distance between the oppositely charge electrodes (in m)
R	Resistivity

Sludge	Mixture of solid wastes and bacteria removed from the wastewater at various stages of the treatment process
TSS	Total suspended solids (in $mg.kg^{-1}$)
VSS	Volatile suspended solids (in $mg.kg^{-1}$)
USEPA	United States Environmental Protection Agency
UASB	Up flow anaerobic sludge blanket reactor
WHO	World Health Organization

LIST OF SYMBOLS

$\mathbf{pH_{zpc}}$	Zero point of charge
$\mathbf{u_{EO}}$	The electroosmotic velocity
$\boldsymbol{\varepsilon}$	Dielectric constant of the pore fluid
$\boldsymbol{\mu}$	Viscosity of the fluid
$\boldsymbol{\delta\phi/\delta\chi}$	Electric gradient
v	The velocity of species in the sand (in $m\ s^{-1}$)
n	Porosity of the lake sand (dimensionless)
u	Mobility of the species (in $m^2V^{-1}s^{-1}$);
$\boldsymbol{\tau}$	Sand tortuosity (dimensionless)
ke	Coefficient of electroosmotic conductivity (in $m^2V^{-1}s^{-1}$)
$\boldsymbol{\Delta\phi}$	Electric potential (in V)

LIST OF ORIGINAL PUBLICATIONS

The thesis consists of seven Chapters as well as five original publications, which are presented by Roman numerals (I - V):

I. **Virkutyte, J.,** Sillanpää M., Latostenmaa P. 2002. Electrokinetic soil remediation – critical overview. The Science of the Total Environment. 289:97 – 121.

II. **Virkutyte, J.,** Sillanpää, M., Latostenmaa, P. and Martišius J. 2004. Electrode layout and process kinetics of electroremoval of copper from sand. International Journal of Surface Mining, Reclamation and Environment, 18:220 – 231.

III **Virkutyte, J.,** Velizarova, E., Ribeiro, A. B. and Sillanpää, M. 2005. Copper and chromium electrokinetic migration in CCA-treated timber waste. Water, Air and Soil pollution. 160:27-39.

IV. **Virkutyte, J.,** van Hullebusch E., Sillanpää, M. and Lens, P. 2005. Copper and trace element fractionation in electrokinetically treated methanogenic anaerobic granular sludge. Environmental Pollution. 138:517 - 528.

V. **Virkutyte, J.,** Sillanpää, M. and Lens, P. 2005. Electrokinetic copper and iron migration in anaerobic granular sludge. Submitted to Water, Air and Soil Pollution.

Contents

CHAPTER 1: ELECTROKINETIC REMEDIATION TECHNIQUE: BACKGROUND OF THE TECHNOLOGY

Virkutyte, J[1]*., Sillanpää M.[1], and Latostenmaa P.[2]

[1] University of Oulu, Water Resources and Environmental Engineering Laboratory, Tutkijantie 1 F 2, 90570 Oulu, Finland.

[2] Finnish Chemicals Oy, P.O. Box 7, FIN-32741 Äetsä, Finland.

* The corresponding author. [Email: jurate.virkutyte@oulu.fi]

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1. Introduction

Contamination of soils and groundwater with different dangerous substances and heavy metals in particular is growing every day. Pollutants most of which are of artificial origins often get released from various sources such as abandoned mining wastes, improper treatment of industrial wastes, leakage from landfills, accidental spills and military activities into the environment and may pose a significant risk to the biota and humans (Kim et al., 2001).

Remediation of contaminated sites is a major technological challenge in a nowadays society. There are numerous remediation technologies available for treating contaminated sites, such as soil vapor extraction, soil flushing, chemical oxidation, soil vitrification, bioremediation, phytoremediation, pump and treat technologies, however most of them may not be both technologically and economically efficient.

While there are many alternatives available, electrokinetic remediation technique offers many advantages for *in situ* treatment of contaminated sites. The main aim of Chapter 1 is to discuss the background, applicability, advantages and technological considerations for electrokinetic remediation technique to treat contaminated soils, timber waste and sludge.

2. Background

Electrokinetic remediation is an innovative technology, which aims to remove heavy metals, organics and radionuclides from contaminated soil, sludge, wood and other contaminated media. It involves an application of a low level direct current (0.15 - 2.3 $mA.cm^{-2}$), which induces the movement of ionic species in the media-water solution towards the oppositely charged electrode (electromigration), a bulk flow of moisture present in the contaminated media from the anode to the cathode (electroosmosis) and a movement of charged particles or colloids in the applied electric field (electrophoresis).

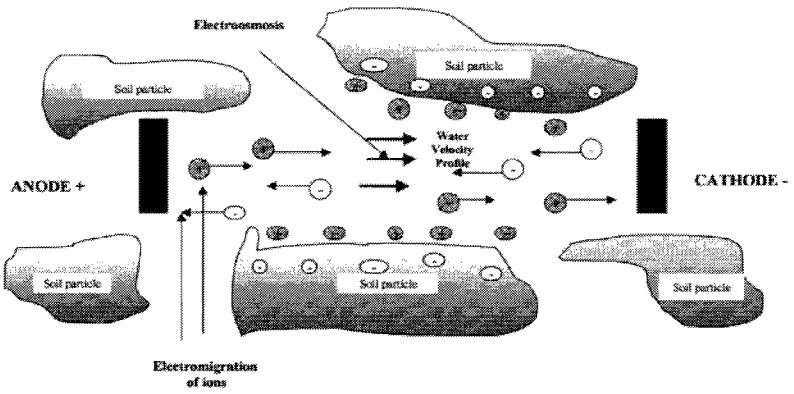

Figure 1.1. Electroosmosis and electromigration of ions (adapted from Acar and Alshawabkeh, 1996)

Electroosmosis is regarded as a rapid flow of pore water and is probably contributing mostly to the efficient remediation of contaminated medium:

$$Q = k_e i_e A \quad (1)$$

where Q is a fluid volume flow rate ($m^3.s^{-1}$), k_e is a coefficient of electro-osmotic conductivity ($m^2.V^{-1}.s^{-1}$), i_e ($i_e = \nabla(-\phi)$, which is electric field strength ($V.m^{-1}$), ϕ is electric potential applied (V) and A is total cross-sectional area perpendicular to the direction of a fluid flow (m^2).

Electromigration is determined as a migration of charged species. According to Alshawabkeh et al. (1999), the rate of species transport under the electric field is:

$$v = (nu\tau + k_e)\nabla(-\phi) \quad (2)$$

where v is a rate of species transport assuming the soil is a homogeneous medium ($m.s^{-1}$), n is porosity of the medium (dimensionless), u is ionic mobility of the species ($m^2V^{-1}s^{-1}$), τ is a factor that accounts for medium tortuosity and species concentration (dimensionless) and k_e is a coefficient of electro-osmotic conductivity ($m^2.V^{-1}.s^{-1}$).

Electrophoresis is the migration of charged colloids, however, electrophoretic movement is sometimes neglected, especially in closed systems, since solid phase is restrained from movement (Pamukcu and Wittle, 1992).

The combination of these three transport phenomena leads to a movement of contaminant ions towards one of the electrodes. The process may be enhanced by the usage of porous membranes to stop penetration of the unfavorable pH front into the contaminated medium (Kim et al., 2005; Lageman et al., 2005), by addition of chemical reagents to increase contaminant removal rates (Altin and Degirmenci, 2005; Ottosen et al., 2005) and other appropriate technological means like conditioning catholyte pH with different enhancing chemical reagents (Zhou et al., 2004) or using the reversing polarity technique to mobilize the metal contaminants (Pazos et al., 2005).

For the first time the term electro-reclamation has appeared in 1936, when there has been an attempt to remove sodium ions from soil under the applied electric current. In addition, since the 1940s, electric current has been used to dewater, i.e. compact soil (USEPA, 1994). Helmholtz and Smoluchowski were the first scientists to propose a theory dealing with the electro-osmotic velocity of a fluid and the zeta potential under an imposed electric gradient (Acar and Alshawabkeh, 1993). Pamukcu and her research group (1992) have derived the following Helmholtz-Smoluchowski equation:

$$uEO = \frac{\varepsilon\zeta}{\mu}\frac{\partial\phi}{\partial\chi} \quad (3)$$

where u_{EO} is the electro-osmotic velocity, ε is dielectric constant of the pore fluid, μ is the viscosity of the fluid and $\delta\phi/\delta\chi$ is the electric gradient (Pamukcu and Wittle, 1992).

Electrokinetic extraction has been used in the former Soviet Union since the early 1970s to concentrate metals and explore for minerals in deep soils. By 1979, research had shown that the content of soluble ions increased substantially in electro-osmotic consolidation of polluted dredging, while heavy metals were not found in the effluent (USEPA, 1995). By the mid-1980s, numerous researchers had realized independently that electrokinetic separation of heavy metals from soils could be a potential remedial option.

3. Electrokinetic phenomenon in soils

As there are several experimental techniques to remediate coarse-grained soils, *in situ* electrokinetic treatment has been developed for contaminants in low-permeability soils. Electrokinetic treatment is applicable in zones of low hydraulic conductivity, particularly with high clay content. Contaminants affected by electrokinetic processes include heavy metals, radioactive species Cs, Sr, Co, U, toxic anions nitrates and sulfates, dense, non-aqueous-phase liquids DNAPLs, cyanides, petroleum hydrocarbons diesel fuel, gasoline, kerosene and lubricating oils, explosives, mixed organic-ionic contaminants, halogenated hydrocarbons, non-halogenated pollutants and poly-nuclear aromatic hydrocarbons.

When DC electric fields are applied to contaminated soil via electrodes placed into the ground, migration of charged ions occurs. Positive ions are attracted to the negatively charged cathode, and negative ions move to the positively charged anode. It has been experimentally proven that non-ionic species are transported along with the electroosmosis-induced water flow. The direction and quantity of contaminant movement is influenced by the contaminant concentration, soil type and structure, and the mobility of contaminant ions, as well as the interfacial chemistry and the conductivity of the soil pore water. The technique relies on several interacting mechanisms, including advection, which is generated by electro-osmotic flow and externally applied hydraulic gradients, diffusion of the acid front to the cathode, and the migration of cations and anions towards the respective electrode (Zelina and Rusling, 1999).

The acid front is carried towards the cathode by electrical migration, diffusion and advection. The hydrogen ions produced decrease the pH near the anode. At the same time, an increase in the hydroxide ion concentration causes an increase in the pH near the cathode. Other mechanisms that greatly affect the electrochemical remediation process are electroosmosis, coupled with sorption, precipitation and dissolution reactions (van Cauwenberghe, 1997). Once the remediation process is over, extraction and removal of heavy metal contaminants are accomplished by electroplating at the electrode, precipitation or co-precipitation at the electrode, pumping water near the electrode, or complexing with ion exchange resins. Adsorption onto the electrode may also be feasible, as some ionic species will change their valence near the electrode depending on the soil pH, making them more likely to adsorb (van Cauwenberghe, 1997). Prediction of the decontamination time is of great importance in order to estimate possible power consumption and to avoid the occurrence of reverse electro-osmotic flow, i.e. from the cathode to the anode, during the process (Baraud et al., 1997, 1998). The phenomenon of reverse electro-osmotic flow is not well understood and should be further investigated.

3.1. Technological considerations

The success of electrochemical remediation depends on the specific conditions encountered in the field, including the types and amount of contaminant present, soil type, pH and organic content (Acar and Alshawabkeh, 1993). For *in situ* conditions, the contaminated site itself and the immersed electrodes form a type of electrolytic cell. Usually, the electrokinetic cell design in laboratory experiments consists of an open-flow arrangement at the electrodes, which permits injection of the processing fluid into the porous medium, with later removal of the contaminated fluid (Sogorka et al., 1998; Reddy and Chinthamreddy, 1999; Reddy et al., 1997, 1999; Zelina and Rusling, 1999).

It seems that there is a controversy as to where electrodes should be placed to obtain the most reliable and efficient results. It is obvious that imposition of an electrical gradient by having inert electrodes results in electro-osmotic flow to the cathode. Many authors propose that positioning of the electrodes directly into the wet soil mass produces the most desirable effect (Acar and Alshawabkeh, 1993; Reddy et. al., 1999; Sogorka et al., 1998). Through seeking improvements in experiments, some researchers tend to place the electrodes not directly into the wet soil mass, but into an electrolyte solution, attached to the contaminated soil, or else to use different membranes and other materials (van Cauwenberghe, 1997; Baraud et al., 1998; Benazon, 1999). Contaminants at the cathode may be removed by electrodeposition, precipitation or ion exchange. Electrodes that are inert to anodic dissolution should be used during the remediation process. The most suitable electrodes used for research purposes include graphite, titanium, platinum, gold and silver. The choice of appropriate soil for electrokinetic remediation process should be made with extreme caution and possible soil pre-treatment experiments should be carried out.

It is reported that with applied electric fields, the most suitable soils for heavy metal remediation are kaolinite, clay and sand (Sims, 1990; Hamed et. al., 1991; Lindgren et al., 1991; Acar and Alshawabkeh, 1993; Probstein and Hicks, 1993; Li et al., 1997).

However, there are arguments whether sand is a suitable media for electrokinetic treatment (electroosmosis) or it is more suitable to be remediated with conventional pump and treat technologies. According to Acar et al. (1995), sand is not suitable for electrokinetic treatment (electroosmosis in particular) because sand has the lowest surface charge density in comparison to silt, kaolinite, illite and montmorillonite. Among other parameters, electroosmotic flow highly depends upon the magnitude of the charge density on the soil surface. Therefore, lower the surface charge density is, smaller the diffuse double layer and lesser the electroosmotic flow is. On the contrary, Li et al. (1997) argued that heavy metals can be removed from sand efficiently by electromigration alone and therefore electroosmotic flow may be neglected. The ground for this statement is that the direction and the rate of electroosmosis depend on pH (Li et al., 1997). Thus, if pH of the sand is neutral or alkaline, electroosmotic flow may be ignored.

As recommended, clay has low hydraulic conductivity, reducing redox potential, slightly alkaline pH, which is suitable for the remediation of several heavy metal contaminants, high cation exchange capacity and high plasticity. Under normal conditions, migration of ions is very slow, but is enhanced by electrical fields or hydraulic pressure. The highest degree of removal of heavy metals over 90% of the initial contaminant has been achieved for clayey, low-permeability soils, whereas for porous, high-permeability soils, such as peat, the degree of removal was only 65% (Chilingar et al., 1997). Laboratory results showed that electrokinetic purging of acetate and phenol from saturated kaoline clay resulted in greater than 94% removal of the initial contaminants. However, this methodology needs to be further investigated, because phenol has been reported to be toxic to humans and the environment species, and the presence of organic matter and carbonates in the soil. The mechanism is also significantly dependent on the pore fluid pH. Moreover, Calace et al. (2005) and Banks et al. (2005) determined that high content of carbonates and organic material in soils decreases the availability of mobile heavy metal forms, which is why the former should be further investigated and taken into the consideration.

During numerous experiments, a decrease in current density was observed (Acar and Alshawabkeh, 1996; Acar et al., 1996; Sah and Chen, 1998; Shrestha et al., 2003; Altin and Degirmenci, 2005). The possible reasons might be as follows: Activation polarization: during the electrokinetic remediation process, gaseous bubbles O_2 and H_2 cover the electrodes. These bubbles are good insulators and reduce the electrical conductivity, subsequently reducing the current. Resistance polarization: after the electrokinetic remediation process, a white layer

was observed on the cathode surface. This layer may be the insoluble salt and other impurities that were investigated, because phenol has been reported to be toxic to humans and the environment.

3.2. Heavy metal removal conditions

Heavy metal interactions in the soil solution are governed by several processes, such as inorganic-organic complexation, acid-base reactions, redox reactions, precipitation-dissolution reactions and interfacial reactions (Sims, 1990).

It has been proven by experiments that when heavy metals (Cu, Zn, Ni, Cd, Pb) enter into basic conditions, they adsorb to soil particles or precipitate as hydroxides, oxy-hydroxides, etc., and in acidic conditions, those ions desorb, solubilize and migrate. However, heavy metals such as Cr and As are mobile under alkaline conditions and precipitate when the pH gets acidic (Reddy and Chinthamreddy, 1999; Sawada etal., 2004).

Another important parameter in the electrokinetic remediation technique is the conductivity, since this, together with soil and pore fluid, affects the electro-osmotic flow rate. The conductivity of soil depends on the concentration and the mobility of the ions present, i.e. contaminant removal efficiencies decrease with a reduction in contaminant concentration (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999; Yeung et al., 1997). This is due to hydrogen ion exchange with cationic contaminants on the soil surface, with release of the contaminants.

As the contaminant is removed, the hydrogen ion concentration in the pore fluid increases, resulting in an increasing fraction of the current being carried by the hydrogen ions rather than by the cationic contaminants. It is possible to conclude that the variables, which have impact on the efficiency of removing contaminants from soils, are: Chemical processes at the electrodes, soil type and structure, saturation of the soil, pH and pH gradients, type and concentration of chemicals in the soil, applied current density and sample conditioning.

In addition, insoluble organics, such as heavy hydrocarbons, are essentially not ionized, and the soils in contact with them are not charged. The removal of insoluble organics by electric field is limited to their movement out of the soil by electro-osmotic purging of the liquid, either with water and surfactant to solubilize the compounds, or by pushing the compounds ahead of a waterfront (Probstein and Hicks, 1993). Ionic migration is the movement of ions subjected to an applied DC electric field. Electromigration rates in the subsurface depend upon (van Cauwenberghe, 1997): Soil pore-water current density, grain size, ionic mobility, contaminant concentration and total ionic concentration.

The process efficiency is not as dependent on the fluid permeability of soil as it is on the pore water electrical conductivity and path length through the soil, both of which are a function of the soil moisture content ((van Cauwenberghe, 1997).

Electroosmosis is the movement of water relative to the soil under the influence of an imposed electric gradient. When there is direct current applied across the porous media filled with liquid, the liquid moves relative to the stationary charged solid surface. When the surface is negatively charged liquid flows to the cathode. Acar et al. 1994, 1996 have conducted numerous experiments and found that this process works well in wet i.e. water-saturated fine-grained soils and can be used to remove soluble pollutants, even if they are not ionic. The dissolved neutral molecules simply go with the flow.

An excess negative surface charge exists in all kinds of soil. For example, many types of clay are anionic, colloidal poly-electrolytes. The surface charge density increases in the following order: sand-silt-kaolinite-illite-montmorillonite. Injection of clean fluid, or simply clean water, at the anode can improve the efficiency of pollutant removal. For example, such a flushing technique using electroosmosis has been developed for the removal of benzene, toluene, trichlorethane and m-xylene from saturated clay (Lageman, 1993). According to that stated

above, the main factors affecting the electro-osmotic transport of contaminants in the soil system are as follows: mobility and hydration of the ions and charged particles within the soil moisture, ion concentration, dielectric constant, depending on the amount of organic and inorganic particles in the pore solution and temperature.

In order to obtain efficient and reliable results, electrokinetic remediation of soil should be implemented under steady-state conditions. It is obvious that during the remediation process, other reactions, such as transport and sorption, and precipitation and dissolution reactions, occur and affect the remediation process. There have been numerous indications of the importance of heat and gas generation at electrodes, the sorption of contaminants onto soil particle surfaces and the precipitation of contaminants in the electrokinetic remediation process (Acar and Alshawabkeh, 1993; Lageman, 1993; Zelina and Rusling, 1999). These processes should be further investigated, because it is believed that they may weaken the removal efficiency for heavy metal contaminants. It is reported that different physicochemical properties of the soil may influence the removal rates of heavy metal contaminants, due to changed pH values, hydrolysis, and oxidation and reduction reaction patterns. In order to enhance the electrokinetic remediation process, several authors recommend the use of a multiple anode system.

3.3. Zeta potential

Most soil particle surfaces are negatively charged as a result of iso-morphous substitution and the presence of broken bonds (Yeung et al., 1997). Experiments have determined the dependence of the zeta potential of most charged particles on solution pH, ionic strength as well as types of ionic species, temperature and type of clay minerals (Vane and Zang, 1997). For water-saturated silts and clays, the zeta potential is typically negative, with values measured in the 10 –100 mV range.

However, if ions produced in the electrolysis of water are not removed or neutralized, they lower the pH at the anode and increase it at the cathode, accompanied by the propagation of an acid front into the soil pores from the anode and a base front from the cathode. This process can significantly effect the soil zeta potential drop in zeta potential, as well as the solubility, ionic state and charge, level of adsorption of the contaminant, etc. (Yeung et al., 1997).

In addition, different initial metal concentrations and sorption capacity of the soil may produce soil surfaces that are less negative, which at the same time may become positive at a pH of approximately the original zero-point charge (Yeung et al., 1997). Similarly, chemisorption of anions makes the surface more negative. Electro-osmotic flow from the anode to the cathode promotes the development of a low-pH environment in the soil. This low-pH environment inhibits most metallic contaminants from being sorbed onto soil particle surfaces and favors the formation of soluble compounds.

Thus, electro-osmotic flow from the anode to cathode, resulting from the existence of a negative zeta potential, enables the removal of heavy metal contaminants by the electrokinetic remediation process. The pH of the soil should be maintained low enough to keep all contaminants in the dissolved phase. Nevertheless, when the pH becomes too low, the polarity of the zeta potential changes and reversed electro-osmotic flow i.e. from the cathode to the anode may occur. In order to achieve efficient results in removing contaminants from soils, it is necessary to maintain a pH low enough to keep metal contaminants in the dissolved phase and high enough to maintain a negative zeta potential (Yeung et al., 1997).

Despite this apparently easily implemented theory, simultaneous maintenance of negative zeta potential and dissolved metal contaminants remains the greatest obstacle in the successful implementation of the electrokinetic soil remediation process.

4. Electrodialysis of CCA-treated timber waste

Recycling of CCA treated wood waste into wood-based composites is believed to be a relatively low-cost alternative to disposal into the environment. However, the leaching of toxic chemicals to the environment is one of the most limiting factors when choosing this alternative. Leaching of CCA chemicals depend on rainfall, pH of the surrounding environment and wood composition. Hence, there is a necessity to find low cost remediation techniques to overcome the leachate and landfilling problems.

The most successful method for recycling CCA-treated wood waste would be to modify it by removing all of the heavy metals so that both the wood fiber and the metals could be reclaimed (Hingston et al., 2001). Suitable CCA-treated timber waste remediation techniques mainly depend on the concentration and physical state of the contaminants as well as on the impregnation procedure and on how strong contaminants are bound to the timber structure.

Electrodialytic remediation is closely related to electrokinetic remediation technique, just ion-exchange membranes are used instead of passive barriers (Ottosen et al., 1997). The advantage of using ion-exchange membranes is to prevent ions from re-entering into the already treated matrix and decrease in current efficiency, which would occur due to the acidic catholyte introduced into the system to control the pH (Kim et al., 2005).

Ribeiro et al. (2000) determined that with low level (0.2 $mA.cm^2$) electric current and 2.5% oxalic acid as enhancement agent, removal efficiencies over 90% for Cu, Cr and As may be achieved.

5. Electrokinetic remediation of sludge

In most cases, industrial sludges with high heavy metal contents are strictly forbidden to be applied on the land. Heavy metals should be removed prior to sludge distribution. This could be done with the help of electrokinetic remediation technique. The basics of the technique are the same as in removing selected heavy metals from soil and CCA-contaminated timber waste. Nonetheless, there are several differences between the treated matrices such as that sludge is 100% saturated with water in comparison to 60-70% saturation of soil and 50-60% of timber waste. Also, fractionation of heavy metals may differ in all three matrices, e.g. heavy metals in soil and CCA-treated timber waste were mostly found in less labile fractions such as iron-manganese oxides, organic/sulfides and residual fractions (Balasoiu et al., 2001; Embrick et al., 2005; Remon et al., 2005). Whereas heavy metals found in the sludge are mostly bound to carbonates and organic/sulfides (Kim et al., 2002). As bonding of heavy metals are different in all the matrices, it is very likely that desorption mechanisms will differ as well.

6. Practical application of electrokinetic treatment technique

6.1. Pilot scale experiments

6.1.1. LasagnaTM process

In 1995, a novel integrated method for in situ electrokinetic remediation of soils, called Lasagna^{TM}, was developed and implemented at the Paducah site, in Kentucky (USA). This technology is useful for removing heavy metal contaminants from heterogeneous, low-permeability soils (Ho et al., 1997). In brief, the Lasagna^{TM} process contains the following concepts:

- The creation of several permeable 'treatment' zones in close proximity through the whole soil matrix by adding sorbents, catalytic reagents, buffering solutions, oxidizing agents, etc.

- Application of an electric current in order to transport contaminants into the 'treatment' zones.

The Lasagna™ process has several advantages in comparison to other techniques. First, it is possible to recycle the cathode effluent by aiming it back to the anode compartment, which would favor neutralizing of the pH and simplify water management. In addition, the fluid flow may be reversed by simply switching the polarity (Ho et al., 1997). The switching of polarity promotes multiple contaminant passes through the 'treatment' zones and helps to diminish the possibility of non-uniform potential and pH jumps in the soil system. Two schematic Lasagna™ model configurations were suggested: a horizontal (Fig. 1.2.a) and a vertical (1.2.b) configuration.

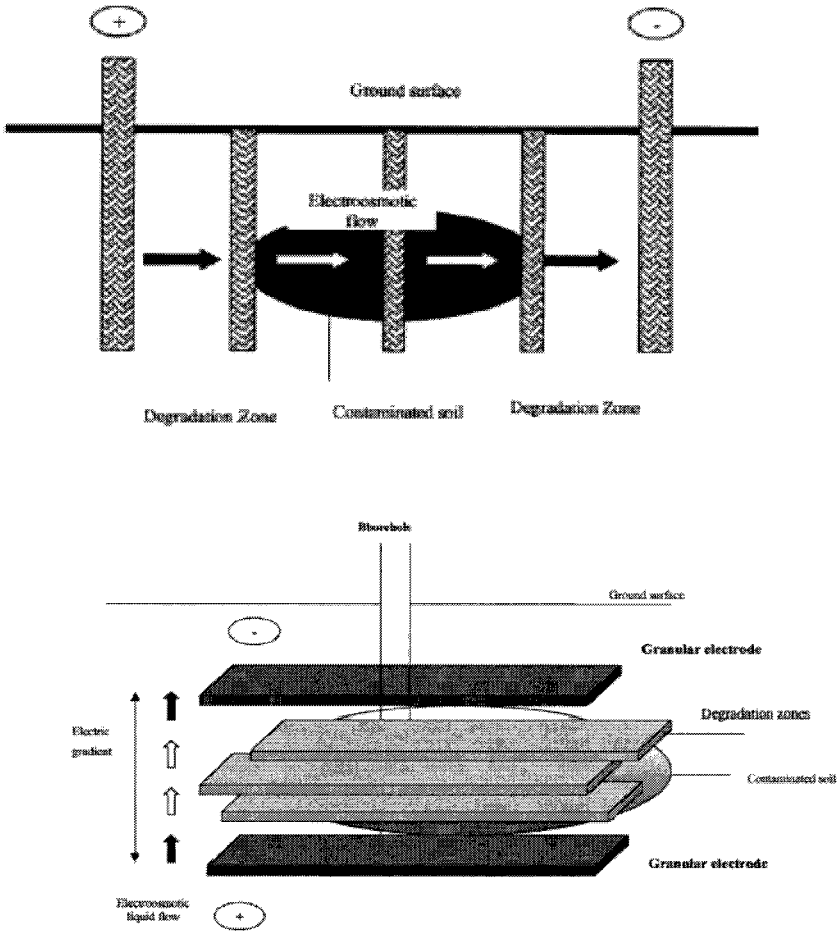

Figure 1.2. Lasagna™ configuration for electrokinetic soil remediation (adapted from Ho et al., 1997)

The process was called 'Lasagna' due to the layering of treatment zones between the electrodes. The formation of horizontal fractures in over-consolidating clays due to the horizontal electrodes and vertical pressuring system make this method especially effective in

removing contaminants from deeper layers of the soil (Ho et al., 1999). In addition, for shallow contaminations, which does not exceed 15 m and in not over-consolidated soils, the vertical treatment configuration (Fig. 1.2b) is more appropriate (Ho et al., 1997). According to laboratory experiments and promising pilot-scale studies at the Paducah site in Kentucky, Lasagna™ technology may become one of the most widely used electrokinetic remediation technologies for removing heavy metal contaminants from various soils.

6.1.2. Electrokinetic bioreclamation

Electrokinetic bioremediation technology is designed to activate microbes and other microorganisms present in soils by the use of selected nutrients to promote the growth, reproduction and metabolism of microorganisms capable of transforming organic contaminants in soil (van Cauwenberghe, 1997). Nutrients reach the organic contaminants by specially applied bioelectric technology. It is believed that this technology may be very successful, because it does not require an external microbial population to be added into the soil system. In addition, nutrients may be uniformly dispersed over the contaminated soil or directed to a specific location (van Cauwenberghe, 1997) and the method avoids the problems associated with transport of microorganisms through fine-grained soils (Fig 1.3). This technique is very time and cost efficient in treating volatile organics, semi-volatile organics, dense non-aqueous phase liquids (DNAPLs), heavy fuel oils, creosote and polycyclic aromatic hydrocarbons (Lageman et. al., 2005). It has been reported by the founder of electro-bioreclamation in Europe Lageman et al. (2005) that electrical heating, which heats the soil with AC or DC currents, does not sterilize the natural bacteria or over-saturates the soil locally; hence heating does not impair the remediation process.

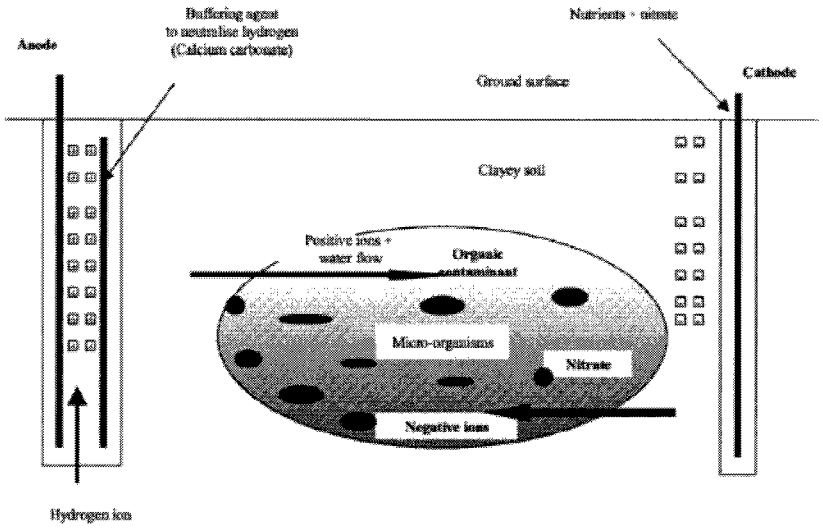

Figure 1.3. Electrokinetic bioremediation (according to Thevanayagam and Rishindran, 1998)

6.1.3. Electrokinetic biofence

Godschalk and Lageman (2005) discovered an alternative for containment and remediation of polluted groundwater plumes - the deployment of electrokinetic biofence (EBF), which aims at removing or stopping migration of volatile organic compounds (VOCs) from / in the groundwater. The main principle of EBF is the employment of a row of three cathodes and two anodes, positioned 5 meters apart from each other. Upstream of a biofence, a series of infiltration wells are installed, which are constantly filled with nutrients like nitrogen, phosphorus, oxygen donors, organic compounds and micronutrients, required for the biodegradation of VOCs (Godschalk and Lageman, 2005).

6.2. Electrokinetic treatment enhancement techniques

In order to have efficient removal of heavy metal contaminants, it is not sufficient only to put electrodes to the conductive solution or directly into the contaminated media and apply low-level direct current. Processes, which take place under the applied electric field and in the contaminated media itself, are so complex that sometimes it impairs remediation processes due to stopped mobility of ions, formed complexes between contaminants or with contaminated media fractions. To overcome those limitations of the technique and raise the removal efficiency, one needs to employ several enhancement methods.

To overcome the premature precipitation of ionic species, Acar and his research group have recommended using different enhancement techniques to remove or to avoid these precipitates in the cathode compartment. Efficient techniques should have the following characteristics (Acar, et al., 1993):

- The precipitate should be solubilized and or precipitation should be avoided.
- Ionic conductivity across the specimen should not increase excessively in a short period of time to avoid a premature decrease in the electro-osmotic transport.
- The cathode reaction should possibly be depolarized to avoid the generation of hydroxide and its transport into the specimen.
- Depolarization will decrease the electrical potential difference across the electrodes, which would result in lower energy consumption.
- If any chemical is used, the precipitate of the metal with the new chemical should be perfectly soluble within the pH range attained.
- Any special chemicals introduced should not result in any increase in toxic residue in the contaminated media mass.
- The cost efficiency of the process should be maintained when the cost of enhancement is included.

6.2.1. Enhancement and conditioning

It is obvious that an enhancement fluid increases the efficiency of contaminated media treatment. However, there is a lack of data, which would clarify further media and contaminant interactions in the presence of this fluid. As a depolarizer i.e. enhancement fluid in the cathode compartment, it is possible to use a low concentration of hydrochloric or acetic acid (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996). The main concern with hydrochloric acid as the depolarizer is that due to electrolysis, the chlorine gas formed may reach the anode, as well as groundwater, and increase its contamination. Acetic acid is environmentally safe and it does not fully dissociate. In addition, most acetate salts are soluble, and therefore acetic acid is preferred in the process. The anode reaction should also be depolarized, because of the

dissolution and release of silica, alumina and heavy metals associated with the clay mineral sheets over long exposure to protons (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996).

In order to accomplish both tasks successfully, it is better to use calcium hydroxide as the enhancement fluid to depolarize the anode reaction, and hydrochloric acid as the enhancement fluid to depolarize the cathode reaction. The use of an enhancement fluid should be examined with extreme care to prevent (Yeung et al., 1997):

- The introduction of a secondary contaminant into the subsurface;
- The generation of waste products or by-products as a result of electrochemical reactions;
- The injection of an inappropriate enhancement fluid that will aggravate the existing contamination problem.

6.3. Electrodes

To have an electric field it is necessary to have two electrodes. Under the applied direct current electrons are released from the anode and are used by the cathode. The dominant and most important electron transfer reactions that occur at electrodes during the electrokinetic process is the electrolysis of water:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2} O_2\,(g) + 2e^-$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\,(g) \qquad (4)$$

Due to the electrolysis of water (in the presence of conductive solution as pure water has no electric conductivity), migration of H^+ and OH^- will drastically change the pH of the system (Yuan and Weng, 2003).

If acid-base indicators are placed in the solution, color changes confirm that the solution becomes basic around the cathode and acidic around the anode as the electrolysis proceeds. In addition, the gases H_2 and O_2 can be collected (Eq. 4).

Polarization of electrodes is the change in potential of both electrodes involved in the electrolysis process. The current density determines the deviation of the electrode potential from its equilibrium value when an external current is passed. The larger the deviation, the slower the electrode reactions are (Ottosen, 1995). The current density cannot be increased beyond a certain critical value without causing a sharp drop in the current efficiency and an equally sharp rise in the energy requirement.

It is extremely important to choose the right electrode material, number, spacing and layout. It will determine the lifetime of the electrodes, possible reactions, magnitude of current strength, etc (Hansen, 1998). According to the electrode reactions, the pH will rise in the cathodic compartment and significantly drop in the anodic compartment due to the formed OH^- and H^+ ions respectively. With employment of the membranes, no OH^- or H^+ ions are allowed to pass into the anodic and cathodic compartments respectively. However, the reduction of heavy metal contaminant ion to the free metal may occur, hence it will be very difficult to control the electrode reactions.

6.4. Conductive solution

As water is a very bad electrolyte, some salts should be used as current transmitters from one electrode to another. Basically ions present in the conductive solution will be transported to the appropriate electrode due to their charge. Many heavy metal species favor acidic environment where they stay in the solution and do not precipitate. Precipitation of metals will impair the

remediation process by decreasing the efficiency of the current transport, hence increasing the resistance over the cell and fouling of the membranes. Therefore, the conductive solution close to the cathode should be kept acidic.

6.5. Membranes

Under the applied direct current, H^+ forms at the anode and OH^- at the cathode hence lowering and raising the pH of the system respectively. The rate at which the hydrogen and hydroxyl ions are produced is fixed by the current and occasionally also by competition of other types of electrode processes (Ottosen, 1995). Without passive membranes, alkaline and acidic fronts meet during the remediation process; hence a sharp pH jump occurs. Acid and alkaline front formation is affected by several factors (Ottosen, 1995): concentration of contaminant ions (copper ions are precipitating on the cathode – less hydroxyl ions will be formed, media composition (if the media contains more lime or organic matter, they would act as buffers and pH changes will not be very sharp) and other ions presents in the contaminated media (H^+ or OH^- ion production will be lower if more ions of the same charge will carry the current).

Ion selective membranes are used to stop selected ions from penetration into the solution or the treated media. Hence, the employment of the cation exchange membrane between the soil and cathode compartment, which prevents negatively charged ions from migrating into the media, therefore allowing heavy metal ions to pass through the membrane into the cathode compartment. On the other hand, anion exchange membrane is positioned in the way to prevent cations from the anode compartment reaching the media, however allowing anions pass into the anodic compartment.

As reported (Hansen et al., 1998), such concept has several advantages:

- There will no flow of electrolytes between two electrode compartments, which minimizes the consumption of the electric power.
- The amount of heavy metal contaminants in the media will be reduced to a minimum until no movable ions are available. However, high resistance may be formed due to the changes in volume and changes in ion concentration.
- If heavy metal has changed its oxidation state in the electrolyte compartment, the new charge is prevented by the ion exchange membrane from re-entering to the medium.

In order to efficiently use the membranes, one needs to remember that cations arriving to the cathode can be reduced on the electrode if the potentials are not controlled sufficiently. Nevertheless, the control of potentials is extremely complicated due to the different species, which arrive to the electrode. Composition and materials of the membranes vary according to their application. Membranes may be polymer based – sulfonated polystyrene (very acidic), polymers with carboxylic acid (weakly acidic) as active groups or Teflon based (polytetrafluoroethylene) membranes for cation exchange and polymers containing tertiary ammonium groups (very basic) or primary, secondary and tertiary amine groups (weakly basic) for anion exchange membranes. They also may be inorganic made of materials such as zeolite (Hansen, 1998).

Important parameters for the overall efficiency of the membrane performance are as follows (Hansen, 1998):

- Electric conductivity and resistance

$$Conductivity = \frac{1}{resis\tan ce} \tag{5}$$

Usually membranes are polar and porous. Hence they are able to conduct the electric current. If the conductive solution is polar, the electric resistance in the membrane decreases. The most efficient membrane should have good conducting properties, therefore maintaining a low electric resistance. If the concentration of ions is higher in the conductive solution, the conductivity raises because there are more ions available to transport the electric current through the membrane. The conductivity depends on the valence of the ion on which the membrane is, i.e. trivalent or divalent cations show much lower conductivity than monovalent cation species (Hansen, 1998).

- Degree of swelling and cross-linking

Degree of cross-linking refers to the feature of polymer chain to be bound together. Commercially available membranes have appropriate degree of cross-linking, which is needed to avoid the dissolution of the membrane and to maintain their stability. If the degree of cross-linking is too high, the transport through the membrane is diminished, i.e. void ratio and water content become too small, which means the diminished electric conductivity through the membrane. From the other hand, too little degree of cross-linking means that membrane may become soluble in the conductive solution and lose the desired features.

- Ion exchange capacity

The ion exchange capacity refers to the feature of the membrane, which is the amount of charges that a membrane is able to exchange per gram membrane (Hansen, 1998). The amount of ionic groups bound in the polymer structure determines the ion exchange capacity. It is obvious that electrokinetic remediation processes favor as high ion exchange capacity as possible, i.e. a better electric conductivity (Hansen, 1998).

- Mechanical and chemical stability

It is very important to have a membrane, which does not change its properties under the applied mechanical or physical stress. The stability of the membrane is usually decreasing with increasing water content, i.e. with swelling. Mechanical stability of membranes usually decreases with aging. In addition, efficient membranes should have a higher chemical stability when in contact with chemical substances. During electrokinetic remediation process, as membranes should be stable under the acid or base, present in the conductive solution, as well as resist organic solvents, chemical compounds and microorganisms influence. Membranes should also be resistant towards fouling.

- Electro-osmotic transport

For successful electrokinetic remediation process, it is more likely to have low electro-osmotic transport of water to keep the original water content in the media volume to avoid compaction or dewatering.

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CHAPTER 2: HEAVY METALS IN SOILS, CCA-TREATED TIMBER WASTE AND SLUDGE

1. Introduction

Properties of contaminated medium may have a strong influence on heavy metal retention and accumulation by different biological and chemical mechanisms resulting in contamination of the environment. Therefore, a good understanding of contamination and assessment of the potential effect of medias contaminated by heavy metals require identification of bonding mechanisms and evaluation of heavy metal retention and potential bioavailability.

The aim of Chapter 2 is to discuss the basic chemistry, availability, distribution and bonding of heavy metals in soil, CCA-treated timber waste and sludge.

2. Heavy metal sources in soils

2.1. Sources of heavy metal pollution

Natural sources of heavy metals are mostly from volcanic activities. However, natural heavy metal concentrations in soils are heavily exceeded by causes of anthropogenic activities, such as (Alloway, 1995):

- Mining and metallurgy industry wastes, i.e. effluents, which contaminate the soil and ground as well as surface waters, gas emissions and landfill sites. Electronics is one of the major environment polluting industries with heavy metals such as Cu, Zn, Ag, Au, Pb, Cr, Co, Hg, etc. These heavy metals are used in the manufacture of semiconductors and other related equipment.
- Urban and industrial wastes containing heavy metals. Heavy metal contamination occurs from batteries (Pb, Ni, Cd, Hg), chlorine manufacture (Hg), pigments and paints (Pb, Cr, As, Cd), medical uses (As, Ag, Cu, Hg, Pb, Zn) and other industrial wastes.
- Combustion of fossil fuels. When combusting the fossil fuels, the atmosphere receives high amount of Pb, Cd, Cr, Zn, As, Cu, Mn and other heavy metals.
- Agricultural and other related activities i.e. soil and water contamination by animal manure (Cd, Cu, Pb, Zn), pesticides (Cu, As, Hg, Pb, Mn, Zn), wood preservatives (As, Cr, Cu) and corrosion of metal objects (Zn, Cd).

According to Pagnanelli e al. (2004), metals, anthropogenically introduced into the environment, are usually present as dissolved in the aqueous phase of soil, occupying exchange sites on inorganic soil constituents, adsorbed on soil surfaces, associated with insoluble soil organic matter and precipitated as pure or mixed solids.

2.2. Heavy metal retention and transformation in the soil

When in contact with soil or water media, contaminants are adsorbed or absorbed to the soil particles or washed into the soil matrix by rainfall or snow. Heavy metals reach the soil and groundwater mostly as solutions. The adsorption mostly occurs in the clay fraction of the soil where the smallest pores are present (Ottosen, 1995). If heavy metal contaminants in the soil are in ionic forms, they are attracted by the static electrical force of negatively charged soil colloids. The attraction of metal ions to the soil colloids primarily depends on the soil electro-negativity and the dissociation energy of ions (Sah and Chen, 1998). If there are appropriate pH conditions, heavy metals are likely to be adsorbed onto the negatively charged soil particles.

The main sorption mechanisms include adsorption and or ion exchange. Desorption of cationic species from clay surfaces is essential in extraction of species from fine-grained deposits with high cation exchange capacity.

Soluble pollutants will infiltrate into the topsoil in the systems of pores where the adsorption of ions occur. Alloway (1995) argued that adsorption and absorption is highly dependent on the pH of the soil, contaminant nature and redox conditions. Mechanisms, responsible for the retention of heavy metals in soils (according to Alloway, 1995):

- Specific adsorption, which involves the exchange of heavy metal cations and most of the anions with surface ligands to form covalent bonds with lattice ions. It is very pH dependant and is related to hydrolysis of heavy metal ions. Under the influence of the specific adsorption, heavy metals in soils are in the form of Me^{2+} ions and MOH^{+}.

$$>Fe\text{-}OH + MOH^{+} \Rightarrow > Fe\text{-}O\text{-}MOH + H^{+}$$

- Organic complexation – humic acids may adsorb heavy metal species by forming different chelate complexes. The stability of formed chelates is decreasing in the order: Cu > Fe (III) = Al > Mn = Co > Zn. In addition, low-molecular weight organic ligands may form soluble complexes with heavy metals, hence preventing them from adsorption or precipitation.
- Co-precipitation – is a simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism at any rate. Usually new minerals are formed as ferrous oxides with traces of Mn, Ni, Cu, Zn or Mo; manganese oxides with traces of Fe, Co, Ni, Zn or Pb; calcium carbonates with traces of Mn, Fe, Co or Cd and clay minerals with traces of V, Ni, Co, Cr, Zn, Cu and other heavy metal species.
- Non-specific adsorption, i.e. Cation exchange – most heavy metals exists in soil as cations in the solution and their adsorption depends on the density of negative charges on the surfaces of the soil colloids. Ion exchange processes refer to the exchange between counter ions and ions present in the solution. In addition, ion exchange also refers to the formation of outer complexes with the surface functional groups to which they are bound electrostatically. The cation exchange capacity increases with increases in pH and anion exchange capacity increases with pH decrease because the solid phase has increased positive charge.
- Surface-OH surface-O^{-} + H^{+}

2.2.1. Heavy metal speciation in soils

The knowledge of chemical heavy metal bonding is essential to characterize the behavior of heavy metals in soils, i.e. it is important in order to assess heavy metal reactivity and hence availability to the environment and their potentially harmful effects (Denaix et al., 1999; Abollino et al., 2002). Several factors affecting the heavy metal speciation in soil systems are ionic strength, Eh, pH, reaction kinetics, concentrations and complexing affinities of cations and anions present in the matrix (Ottosen, 1995).

Figure 2.1 presents selected heavy metal species distribution under different redox and pH conditions.

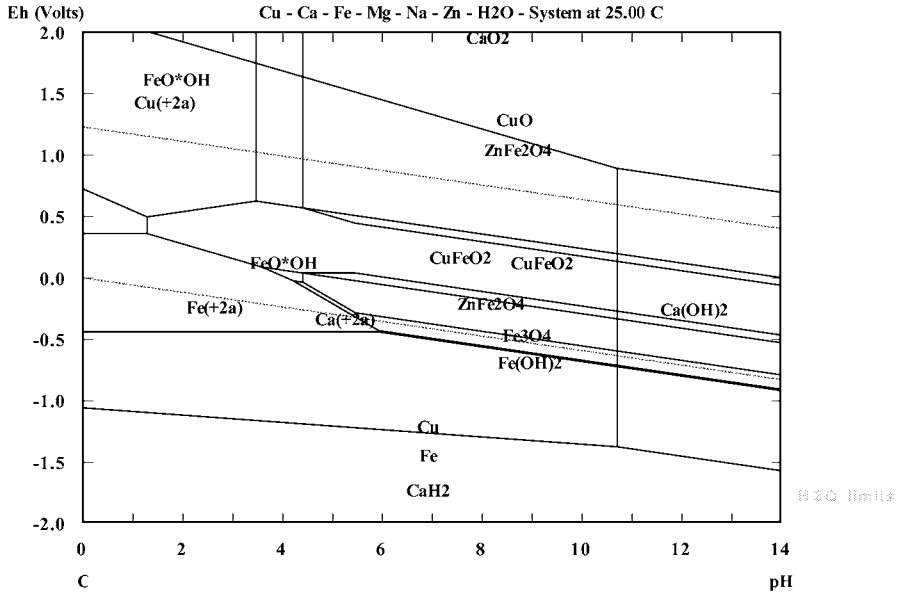

Figure. 2.1. Eh-pH diagram of selected heavy metals.

Most heavy metals undergo redox reaction when present in the soil environment. According to the Eh-pH diagram produced by the author of the thesis (Figure 2.1), when strongly reducing conditions present at low pH, the main species are free ions, e.g. Cu^{2+} and Fe^{2+}. On the other hand, with an increase in pH and Eh, hydroxides and complexes prevail such as $Cu(OH)_2$, $Fe(OH)_2$ and $CuFeO_2$.

Cancès et al. (2003) determined that bioavailability and the potential toxicity of heavy metals in the environment depend on their chemical bonding in the soil and the soil solution. For example, Cd and Zn are mostly found in solution as free aqua-ions and their bonding is mainly controlled by Fe and Mn oxides, Cr and Cu are mostly associated with the dissolved organic matter and Fe, Ni and Zn were found in the residual mineral fraction and Mn was found to be uniformly spread among all the fractions (Adamo et al., 2003). However, there seems to be a controversy between researchers whether for example Pb has stronger affinity for organic matter (Cancès et al., 2003) or more bind to residual fraction (Adamo et al., 2003) in soils.

When sediments were analyzed close to the mining activities, it was found that Fe and Pb are mostly bound to residual phase (Pagnanelli et al., 2004; Ramirez et al., 2005). Ramirez et al. (2005) also detected Cd, Mn, Ni and Zn mostly in the residual fraction. However, Pagnanelli et al. (2004) argued that Mn is mostly complexed onto Fe and Mn oxides and sulfides and Zn is more associated with sulfide phase.

3. Cu in soils

As essential element, Cu is required by organisms for a wide range of metabolic processes and it is considered to be a prototype for the emergence of biologically important functional systems. Metal deficiency is associated with a number of physical and physiological problems in humans. They are as follows (Mercer, 2001):

- Energy metabolism and body composition;
- Physiological dysfunction;
- Resistance to toxic compounds;
- Cell metabolism;
- The chemistry of cell products.

Since high levels of Cu are hazardous for biota it is important to control its amount in the environment, especially the amount, which has reached the environment via artificial performances. Cu is found in rocks like basic igneous (basaltic), acid igneous (granites), shales and clays, volcanic rocks, limestones and sandstones (Alloway, 1995).

The amount of Cu in basaltic rocks is much greater than in acidic, i.e. granitic rocks with very low in carbonate rocks. According to Alloway (1995), the abundance of Cu in igneous rocks is party due to the process of differentiation during crystallization. Main sources of Cu in the environment are as follows:

- Agricultural and related practices. Cu reaches the soil as pesticides (blue stone $CuSO_4 \times 5H_2O$), fungicides (foliage spray). In addition, livestock manures and sewage sludges contain high amounts of Cu as it is used as a food additive.
- Atmospheric deposition.
- Sewage sludges. More than two thirds of all Cu effluents (mainly from household plumbing) in sewage remain in the sludge.
- Other point and non-point contamination, i.e. by fly ash captured from the burning of coal for electricity generation, from the combustion of wood products, fossil fuels and waste incineration.
- Contamination from smelters via effluents and soil erosion.

When entered into the environment, artificial Cu remains mainly adsorbed in the top layer of the soil. Cu can exist in soil solution, ionic and complexed forms, in the soil oxide materials, in organic residues and in the lattice structure of primary and secondary minerals. In saline environment, sulfates and chlorides can form complexes with Cu^{2+}. The behavior of Cu in soil is dependent on soil pH, organic matter content, the presence of iron, manganese and aluminum oxides, and clay soil mineralogy. (Yaron, et al., 1996).

Figure 2.2 shows the computer-simulated Cu species distribution in the presence of major anions.

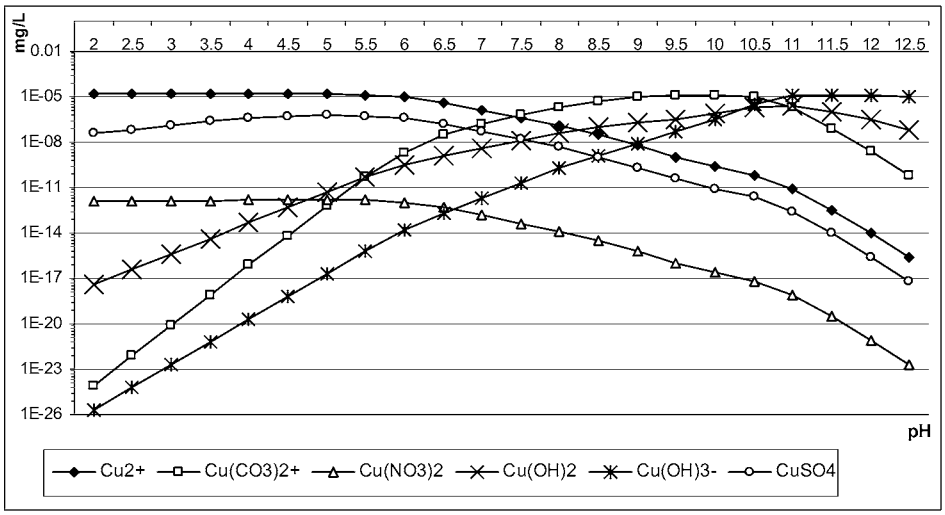

Figure 2.2. Cu species distribution at different pH.

The most toxic species of Cu is Cu^{2+}. As depicted in Figure 2.2, the main Cu species in aquatic solutions at acidic pH are Cu^{2+}, $CuSO_4$ and $Cu(NO_3)_2$. Slightly alkaline pH conditions are favored by $Cu(CO_3)_2^{2+}$, $Cu(OH)_2$ and in lesser extend Cu^{2+}. However, when pH gets extremely alkaline, the main Cu species are $Cu(OH)^{3-}$, $Cu(OH)_2$ and $Cu(CO_3)_2^{2+}$.

Together Cu and humic acids can form strong solution complexes in soils. When pH increases and ionic strength decreases, the affinity of Cu for humates increases. Cu can also form CuS in anaerobic and sulfur rich environments. The mobility of Cu can be decreased by sorption to mineral surfaces (Evanko & Dzombak, 1997).

$$\text{Log } Cu^{2+} = 2.8 - 2\ pH \qquad (6)$$

According to Alloway (1995) soil-Cu may be cupric ferrite. In most agricultural soils at the pH above 5.5, Cu is present as specifically adsorbed ions or complexes. When added to the soil, Cu may undergo hydrolysis, inorganic complexation and / or organic complexation. When the pH is below 6.9 Cu is in the form of Cu^{2+}, and when the pH is above 7, Cu is in the form of $Cu(OH)_2^0$. The adsorption by weight of Cu^{2+} to clays are in the order: kaolinite > fireclay-type kaolinite > illite > smectite (Alloway, 1995). It refers to the fact that Cu^{2+} adsorption increases as the silica sesquioxide ratio in the soil decreases. In addition, Cu^{2+} adsorption does not directly depend on the cation exchange capacity of the clay but highly depend on the pH.

4. Origin of CCA-treated timber waste

Water-born chromated copper arsenate (CCA) has been a major wood preservative for more than 50 years for many applications, such as impregnated telephone poles, railway sleepers, cooling towers, wooden silos, hop-poles, cable drums and wooden play ground equipment. CCA is the most efficient wood preservative due to its excellent fungicidal (Cu) and insecticidal (As) properties (Dawson et al. 1991). In Finland, CCA preservatives have been used as wood preservatives since at least the 1950s. The use of CCA as wood preservatives have caused widespread metal contamination in soils in many countries around the wood preservation sites

due to raw material handling, spills, deposition of sludge and dripping from freshly impregnated wood or due to leaching from the piles of impregnated wood at these sites by rain water especially under low pH conditions (Bhattacharya et al, 2002).

After usage CCA-treated timber may be disposed at landfills or incinerated in commercial kilns. However, there is an increased concern about the possible contamination of the surrounding environment and threat to human health. It is reported that with an expected average service life between 9 and 50 years, disposal of CCA-treated waste wood will pose a major environmental problem in the future when it is removed from service (Kartal, 2003). According to the EU directives, until 1999 pressure treated wood, i.e. CCA treated wood taken out of service is not regarded as hazardous waste and is placed into the municipal landfill (Bjorklund et al., 1998). Though in 1999, EU Directive 31/CE/26/4/99 implies that biodegradable waste cannot be placed into landfills without a pretreatment.

Placement of impregnated wood residue without the pretreatment into the landfills may pose a significant risk to the environment, especially to the groundwater and soil. However, it is declared that water based CCA-preservative treated wood pose less risk for the environmental contamination in comparison to the preservative chemicals prior to application (Bergholm et al., 1992). CCA chemicals are strongly bound to the wood and usually do not leach into the environment, but from the other hand, soil pH and temperature, pressure and soil type may influence the leachate of chemicals to the surrounding environment. Leaching may occur from the surface as well as the fissures within the impregnated wooden stakes due to drying and sunlight exposure.

4.1. Chemistry of CCA constituents

CCA is generally applied to wood by pressure treatment. Instead of applying the chemical to the surface of the wood, the wood is submerged in a cylindrical tank containing the preservative that is then subjected to high pressure to force the CCA into the cells of the wood. Various mixtures of salts can be used to make CCA so that its precise molecular composition may vary from formulation to formulation. However, CCA usually consists of CuO (from 18.1 to 19.6% of Cu), CrO_3 (35.3 to 65.5% of Cr), As_2O_5 (16.4 to 45.1% of arsenic) and H_2O (approximately 24.6% of water). The Cr is used to fix the Cu and As in the wood. In the treatment of wood, up to 250 liters of CCA solution per cubic meter of wood is applied under high pressure, resulting in Cu, Cr, and As wood concentrations in the range of 1000-5000 mg/ kg (Aceto et al., 1994, Dawson et al., 1991). In CCA Arsenic usually is trivalent or pentavalent (pentoxide). Cr is usually either trivalent, or hexavalent, Cr (VI) (Cox, 1991).

CCA-treated timber waste may have different retention value, or mass of CCA chemical used to treat a volume of wood (kg CCA/m^3 wood). Retention values range from 4 to 40 kg/m^3. Lower retention values are suitable for aboveground applications but higher retention levels are necessary for wood foundations, structural poles, piling foundations, and immersion in saltwater (Solo-Gabriele, et al., 2002). Bioavailability of these metals in contaminated soils may vary according to pH, redox conditions and the quantity of organic matter in the soils, and due to changes in the land use pattern. The mobility of the metals is generally controlled by precipitation, diffusion, volatilization and dissolution of unstable minerals, besides other surface complexation processes (Kabata-Pendias et al., 2001). The sorption of anionic contaminants such as As differs significantly from those of cationic contaminants Cu, Cr and Zn depending on soil pH and redox conditions (Eh).

The fate of CCA contaminants thus varies widely in soil environments (Bhattacharya et al., 2002). During the impregnation process, the reaction of Cr (VI) involved an initial adsorption by carbohydrates, reduction and the formation of various complexation reactions such as $CrAsO_4$ with lignin, Cu^{2+} precipitation and complexation with lignin and cellulose and CrO_4^{2-}

complexation with lignin (Pizzi, 1983). Successful preservation of wood depends on several parameters, including magnitude and duration of the process, pressure and temperature as well (Cooper, 1994).

The ratio of preservative components in CCA is crucial to allow rapid and complete fixation and, hence, it is important in order to understand and evaluate the leaching of chemicals into the surrounding environment. It has been reported that the relationship between the Cr : As ratio and total metal leachability exists (Hingston et al., 2001), and a ratio of Cr : As of 1–1.30 as optimum for the most efficient leaching has been proposed. In addition, a Cr : As ratio of 1.9 or greater for maximum As fixation has also been determined. Hence, the premature leaching of As is usually due to insufficient Cr available for complexation (Fahlstrom et al., 1967).

Leaching of CCA chemicals is a very complex, though important, parameter in order to assess the possible hazard for the environment. However despite its importance, leaching of chemicals from CCA preserved wood is not well investigated though it is believed that leaching of chemicals is favored in acidic conditions. It is not clear whether heavy metals leach as individual elements, as Cu and Cr arsenates, as inorganic complexes or even as organo-metallic complexes bound to water-soluble wood extractives (Hingston et al., 2001). Additionally, several researchers propose that Cu is usually bound to low and high organic carbon compounds and Cr to high organic carbon compounds. They make soluble Cu hydroxide ions, CrO_3, $HCrO_4^-$ or $CrAsO_4$ (Baldwin et al., 1996).

4.1.1. Cu

As it was mentioned before, during the preservation of wood with CCA, Cu mainly makes coarse deposits of Cu on cellulose micro-fibrils and several precipitates. Despite Cu is an important micronutrient; it is toxic in the free ionic state Cu^{2+} in high concentrations (Shrivastava and Banerjee, 1998). When there are favorable conditions, leaching of Cu from preserved wood waste into the soil environment and into the groundwater may occur.

The solubility and mobility of Cu is controlled by the pH in the media and redox conditions. When the pH is 5.4 – 6.5, Cu tends to be mobile under oxidizing conditions rather than under reducing conditions (Bhattacharya, et al., 2002). Cu is usually strongly bound to the organic ligands and phenolic groups (Tipping, 1993). If the environment in the soil adjacent to the timber waste becomes alkaline, Cu organic complexes start to leach into the soil and further into the groundwater and may result in heavy contamination with heavy metals.

4.1.2. Cr

Three thirds of the all-annual Cr production is used in alloys, including stainless steel, which contains Fe, Cr and Ni in various proportions, in refractory brick for lining furnaces and kilns production and chemical industries, i.e. chrome alum for tanning leather, pigments and wood preservatives (Alloway, 1995).

The fixation of CCA to a wood matrix is a very complex and active process. During the process, the reduction of the reactive and mobile Cr (VI) to Cr (III) is crucial in the formation of insoluble complexes in CCA-treated wood (Kazi and Cooper, 2005). Usually, Cr makes complexes with lignin, present in the wood, hence, wood with high content of lignin is considered to perform better preservation (Pizzi, 1983).

If leached from CCA-treated timber wastes, Cr can be found at various soil depths due to its oxidation states and complexing agents. The reactions of Cr in soil include oxidation, reduction, and dissolution in the soil pore water, adsorption on the mineral and organic solid phase, and chelation by an organic ligand and precipitation as insoluble compounds. In an alkaline soil, the reduction of Cr (VI) to Cr (III) is slower than in neutral or acid soil compounds. The factors that

affect Cr behavior in soil include pH, oxidation state and electron donors or acceptors. The pH increases the solubility in the aqueous phase and affects the reduction rate. Electron donors or acceptors affect the reduction processes or enhance the oxidation. Some of the organic acids in soil can act as chelator for Cr (III) or as electron donors for Cr (VI). (Yaron, et al., 1996).

The adsorption of Cr (VI) increases with decreasing pH due to the protonation of surface hydroxyl groups on mineral solids (Bhattacharya et al., 2002). It is reported that the reactions that take place in the wood during the fixation of CCA have a great influence on the metal species that are emitted from the wood and the subsequent toxicity of these leachates.

Cr exists in soils as Cr (III) when conditions are anaerobic, redox potential and pH are low.(Yaron, et al., 1996). Soil organic matter can reduce the oxidation state from VI to III. Cr (VI) being a strong oxidising agent is found most often linked to oxygen as chromate ($Cr_2O_4^{2-}$) or the dichromate ($Cr_2O_7^{2-}$). Both of those species precipitate readily in the presence of metal cations, and adsorb on soil surfaces (iron and aluminium oxides). Cr (VI) is tending to be more mobile than the Cr (III). As pH increases, the leachability of soluble and un-adsorbed Cr (VI) increases and hence may contaminate the ground water (Evanko & Dzombak, 1997).

At low pH (<4) the Cr (III) is the dominant form. It forms complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-} and soluble organic ligands (Evanko & Dzombak, 1997). Cationic Cr (III) can be converted to Cr (VI) anions by manganese oxides in moist and aerobic soils (Bartlett & James, 1979). The Cr (VI) anions can be further adsorbed by soil colloids or reduced to Cr (III) by soil organic matter.

Hexavalent forms of Cr can be removed from soils by anion adsorption, precipitation, or by reduction to low-solubility cationic forms. Hexavalent Cr adsorbs better at high pH values, while trivalent Cr precipitates above pH 5.5. (Hsieh et al., 1989). Humans may be exposed to soil-borne Cr by inhalation, oral and dermal contacts. Additional exposure may occur as the result of fate and transport of Cr through leaching into the groundwater, uptake into vegetation and other environmental matrices (Felter and Dourson, 1997). Exposure to Cr (VI) by inhalation can cause cancer toxicity, pulmonary and nasal disruption and by dermal contacts – allergies and dermatitis.

Figure 2.3 presents Cr species distribution under different redox and pH conditions.

When there are strongly reducing conditions, the major species of Cr is CrH, independently from pH and in lesser extend $Cr(OH)_4^-$ when the pH is extremely alkaline (Figure 2.3). However, when oxidizing conditions prevail, at acidic to neutral pH, most abundant species are Cr^{3+} and $Cr_2O_7^{2-}$. Additionally, at alkaline pH, CrO_4^{2-} species prevail.

Air-dry treatment, extractability of Cr (VI), reaction pH, Eh, Cr (III) concentration, reaction time, carbon content, and reactive Mn content affect Cr oxidation.

$$Cr^{3+} + 3MnO_2\,(s) + 4\,H_2O \rightarrow HCrO_4^- + 3MnOOH\,(s) + 4\,H^+ \quad (7)$$

$$MnOOH + 0.55\,O_2 + H^+ \rightarrow MnO_2 + H_2O \quad (8)$$

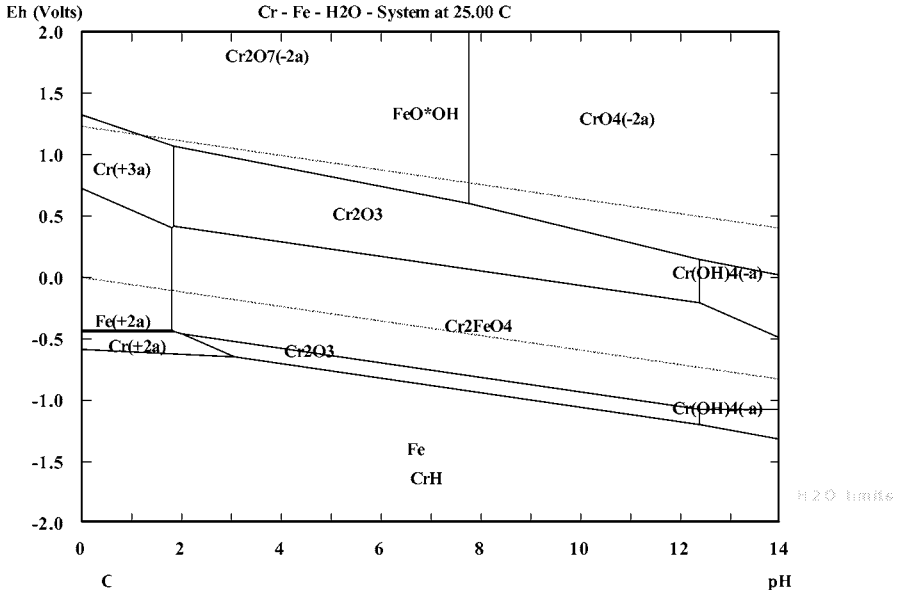

Figure 2.3 Eh-pH diagram of Cr.

MnO_2-mediated Cr (III) oxidation can cause the initial increase in effluent concentrations of Cr (VI). At the same time the accumulation of MnOOH inhibits the Cr (III) oxidation and promotes the decline in Cr (VI) concentrations. The temporal variability in Cr (III) oxidation kinetics can be described within three stages: rapid conversion of Cr (III) to Cr (VI), short interval of declining oxidation rates, and stabilization of transformation rates at low levels. In natural environments, the oxidation of trivalent Cr is more likely to proceed instantaneously compared to the solute residence time. This means that the extent of transformation of trivalent Cr to hexavalent form is limited by the availability of un-reacted MnO_2, but not by the rate of reaction (Guha et al., 2001).

Cr shows a completely different behavior in aquatic environments under the same pH conditions as Cu. Figure 2.4 shows the computer-simulated Cr species distribution in the presence of major anions.

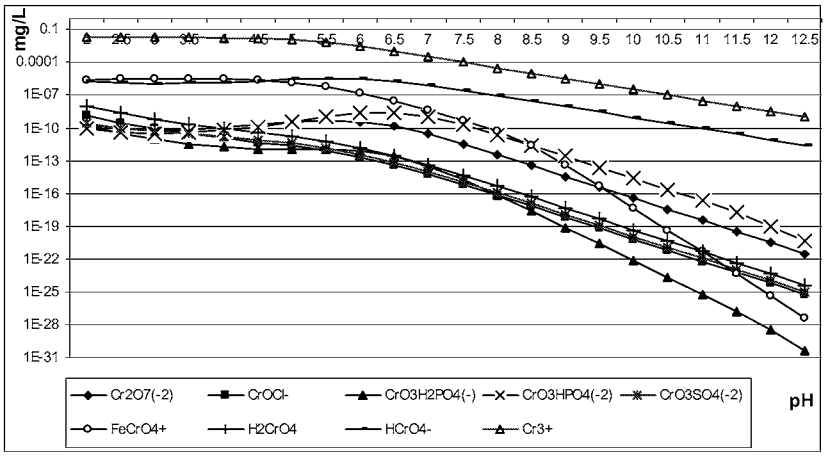

Figure 2.4. Cr species distribution at different pH.

According to Figure 2.4, the availability of Cr species in the aquatic environments decreases with an increase in pH values. Therefore, the major Cr species at acidic pH are Cr^{3+}, $FeCrO_4^+$ and $HCrO_4^-$. When there are alkaline conditions, Cr3+ and $HCrO_4^-$remain the most abundant species, followed by $CrO_3H_2PO_4^-$ complex and $Cr_2O_7^{2-}$. The solubility of Cr (III) decreases above pH 4 and precipitation above pH 5.5 occurs. Cr (III) may become a problem in Mn (III/IV)-rich environments where it can be oxidized to Cr (VI). Cr (VI) is quite mobile in soils and aquifers, whereas Cr (III) is usually associated with solids. However, Cr (VI) can also precipitate as moderately-to-sparingly soluble Ba, Ca, Fe, or Pb salts and can adsorb on sesquioxides at low pH (Yaron, et al., 1996). These solid and immobile forms of Cr (VI) are not readily accessible to reductants and may cause problems in remediation (Reddy and Chinthamreddy, 1999). Oxygen and nitrogen ligands can coordinate with the trivalent form of Cr easily, which is due to Cr tendency to co-ordination.

5. Origins of the sludge

Sludge is a mixture of solid wastes and bacteria removed from the wastewater at various stages of the treatment process. It can be categorized as "primary sludge" and "secondary sludge". Industrial or domestic wastes first receive primary treatment where solids are removed by settling, flocculation or sedimentation. Primary sludge contains about 4% solids and 96% water. It consists of the material, which settles out of wastewater in the primary sedimentation tanks, before bacterial digestion takes place. Secondary or activated sludge has a lower solid content, i.e. about 1% solids and 99% water. Secondary sludge consists of bacteria and organic materials on which the bacteria feed. About 30% of the secondary sludge produced is returned to the aeration tanks to assist with the biological process of sewage treatment. The remaining 70% must be disposed off.

Trickling filters activated sludge processes and attached growth systems are used in secondary treatment. These sludges have a solids content of only 0.5-2%. In the future, many treatment plants will be producing sludges using tertiary treatment such as chemical precipitation and filtration, in which lime and polymers are used to thicken and de-water sludges or other sludge treatment methods, such as electrokinetic or bio-electrokinetic.

Very rarely only domestic sewage goes into treatment plants; industrial effluents and storm-water runoff from roads and other paved areas are frequently discharged into sewers. Thus sewage sludge will contain, in addition to organic waste material, traces of many pollutants used in our modern society. Some of these substances can be phytotoxic and some toxic to humans and/or animals so it is necessary to control the concentration in the soil of potentially toxic elements as well as the rate of the application of the sludge to the soil.

5.1. Heavy metals in sludge

Heavy metals are usually found in effluents from electroplating, galvanic and wood preservation industries, tanneries, also from manufacturing of plastics, paints, refractories and scientific instruments (Chua et al., 1999). Heavy metals occur in sludges in various abiotic physicochemical forms such as, soluble, adsorbed, exchangeable, precipitated, organically complexed and residual phases. In addition, speciation of heavy metals and available forms influence their mobility and potential for environmental contamination. It has been reported that if heavy metal contaminants are in soluble, exchangeable or adsorbed forms they may be mobilized and dispersed. However if they are bound to organic matter or are incorporated into the crystal lattices, it is extremely difficult to separate or mobilize them (Kim, et al., 2002). Table 2.1 presents the concentration of the most important heavy metals in sewage sludge.

Table 2.1. Heavy metals present in the sludge (Alloway, B. J. and Jackson, A. P., 1991)

Element	Chemical symbol	Concentration range (mg/kg dry wt)
Arsenic	As	3 -30
Cadmium	Cd	< 1 - 3410
Chromuim	Cr	8 - 40600
Cu	Cu	50 - 8000
Mercury	Hg	0.1 - 55
Nickel	Ni	6 - 5300
Lead	Pb	29 - 3600
Zink	Zn	91 - 4900

5.1.1. Speciation of heavy metals in sludge

Heavy metals in sludge may be incorporated in the particles or exist in the mobile fraction. Metals in immobile fraction may be sorbed to organic matter, Fe, Al or Mn oxides, and other sludge constituents or precipitated with sulfides, hydroxides, carbonates, and phosphates. Metals in the mobile fraction may be complexed with inorganic soluble ligands, i.e. hydroxides, sulfides, nitrates etc or organic soluble molecules (Langenbach, 1994).

It is well documented that Cu strongly complexes to sludge and it occurs mainly in the organic phase (Su and Wong, 2004; Fuentes et al., 2004; Amir at al., 2005). This means that only a small fraction of the Cu will be found in the solution as ionic Cu (Cu^{2+}). Speciation and mobility of Cr highly depends on the pH of the environmental media as well as on the redox potential (Liu, et al., 1996). Cr (III) species are stable and mobile under the moderate pH conditions and exist mostly in the cationic form. However Cr (VI) has limited mobility under the moderate pH conditions and is more stable under the oxidizing environments and exists mainly in the anionic form (Liu, et al., 1996). Mobility of Cr (III) species is limited in basic

environments due to formed insoluble $Cu(OH)_3$, whereas Cr (VI) mobility under the same conditions is governed by adsorption / desorption reactions (Weng et al., 1994).

6. Summary

Table 2.2 presents the differences of heavy metal bonding to soil, timber waste and sludge.

Table 2.2. Heavy metal bonding in three experimental matrices (according to Evanko & Dzombak, 1997; Kim et al., 2002; Cancès et al., 2003; Adamo et al., 2003; Pagnanelli et al., 2004; Fuentes et al., 2004; Su and Wong, 2004; Ramirez et al., 2005)

	Cu	Cr	Ni	Fe	Zn	Pb	Cd
Aerobic stabilized sludge	organic/sulf.	resid.	resid.	resid.	organic/sulf.	organic/sulf.	organic/sulf.
Anaerobic stabilized sludge	organic/sulf.	organic/sulf.	resid.	resid.	organic/sulf.	resid.	organic/sulf.
Sewage sludge	organic/sulf.	N/A	oxides	N/A	oxides	organic/sulf.	N/A
Municipal sludge	organic/sulf.	resid.	N/A	N/A	N/A	organic/sulf.	resid. and oxides
Soil	organic/sulf.	organic/sulf.	resid.	resid.	oxides	residual organic/sulf.	oxides
Soil close to mining activities	N/A	N/A	resid.	resid.	resid organic/sulf.	resid.	resid.
CCA treated timber waste	organic	organic resid.	N/A	N/A	N/A	N/A	N/A

Apparently, the matrix does not have any effect on Cu and Fe bonding, however bonding of Cr, Ni, Zn, Pb and Cd is strongly influenced by, among other parameters, the effect of the matrix (Table 2.2). The differences in the fractionation may be attributed to different matrix properties, specific interaction between the contaminant mechanisms and the surface and experimental conditions. According to Table 2.2., Zn and Cd are the most difficult metals to predict their speciation. Thus it warrants further research, which takes into consideration the importance of bonding mechanisms, which is vital in order to assess the most feasible and specific site remediation option.

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CHAPTER 3: ELECTODE LAYOUT AND PROCESS KINETICS OF ELECTROREMOVAL OF COPPER FROM SAND

Virkutyte, J.[1]*, Sillanpää, M.[1], Latostenmaa, P.[2] and Martišius J.[3]
[1] University of Oulu, Water Resources and Environmental Engineering Laboratory, Tutkijantie 1 F 2, 90570 Oulu, Finland.
[2] Finnish Chemicals Oy, P.O. Box 7, FIN-32741 Äetsä, Finland.
[3] Vilnius Pedagogical University, Faculty of Natural Sciences, Department of Chemistry Studentu 39, Vilnius, Lithuania
* The corresponding author. (Email: jurate.virkutyte@oulu.fi)

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Abstract

This research paper concentrates on the efficiency of electrokinetic remediation of Cu contaminated sand employing different electrode material, number and spacing. Various electrode number and spacing helps to reduce the remediation time, helps to diminish an inefficient electrical field distribution and helps to also aim to reduce the remediation time. The importance of electrode material such as silver and graphite, the number and the layout for the overall remediation efficiency and time was investigated and evaluated. Experiments with one, two and three one-dimensional anode system has proved that remediation efficiencies as high as 91% may be reached.

Keywords: electrodes, electrokinetics, soil, Cu, remediation.

1. Introduction

Contaminated soils pose serious hazards for the environment and human health. Electrokinetic soil remediation offers a way to remove heavy metals as well as other pollutants from saturated and unsaturated low and high permeability fine-grained soils at minimal expense. When the direct current is applied to the system, positively charged ionic species move toward the cathode while negatively charged species gravitate towards the anode. This movement of charged species is highly dependent on several factors, including pH, redox potential and ionic concentration (Mattson et al., 2000; Chen and Murdock, 1997; Alshawabkeh and Acar, 1996). Once they reach the electrodes, heavy metals and other pollutants may be removed by pumping, electroplating, precipitation or any other applicable method.

For the practical application of electrokinetics, it is necessary to improve not only the efficiency of the remediation process itself, but also to decrease remediation time, both of which will result in the reduction of the overall cost of the technique. One very important factor in increasing the remediation efficiency as well as minimizing process costs and reducing time is to choose the most suitable electrodes, their number and spacing. Optimal electrode spacing and geometry help to achieve the highest remediation efficiencies because the inactive electric field is eliminated, contaminants move faster towards the appropriate electrode where they are subsequently removed (Alshawabkeh et al., 1999).

In the current study, the effect of different electrode materials, number of electrodes, spacing, and geometry on the overall efficiency of electrokinetic technology is assessed. The porous sample media chosen for the experiments is artificially contaminated lake sand, which is the ideal media to assess the electromigration and overall applicability of electrokinetic technology for contaminated sands.

2. Materials and Methods

Laboratory scale experiments were conducted in triplicates with artificially contaminated lake sand and the given results are the mean values of the experiments. The sand was contaminated with 300 mg/kg of Cu, which were evenly distributed along the sand specimen. 'Total' amount of Cu were analyzed according to the BCR reference material (The certification of the extractable contents of Cr, Cd, Cu, Ni, Pb and Zn in freshwater sediments following a sequential extraction procedure, BCR-701, 2001).

All experiments were conducted in the electrokinetic cell developed at the University of Oulu. This electrokinetic cell consists of three compartments, i.e. contaminated sand, which is followed by anodic compartment, membrane and cathodic compartment. The cathode

compartment usually consists of cathode, placed into the catholyte solution and cation exchange membrane. The basic principles of the electrokinetic cell are presented in Figure 3.1.

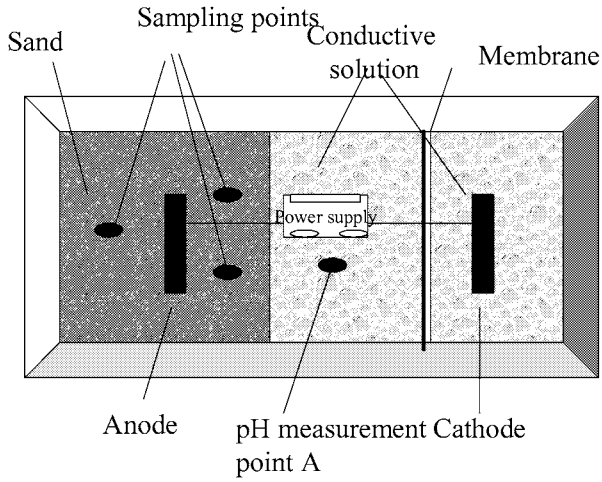

Figure 3.1. The 'open' electrokinetic cell (view from above).

Table 3.1. shows the experimental conditions for the experiments.

Table 3.1. Experimental conditions.

Parameter	Value
Distance between electrodes (cm)	27
Length of the soil (cm)	15
Depth of the remediated soil (cm)	4.4
Mass of the soil sample (g)	1000
Total humidity before experiments (%)	45±2
Total humidity after the experiments (%)	90±2
Bulk density ($g.cm^{-3}$)	1.3
Particle density ($g.cm^{-3}$)	2.65
Porosity (%)	51±2
Medium sand (0.25 - 0.5 mm) (%)	60
Coarse sand (0.5 - 1.0 mm) (%)	30
Fine sand (0.125 - 0.25 mm) (%)	5
Very coarse sand (1.0 - 2.0 mm) (%)	4
Very fine sand (0.05 - 0.125mm) (%)	1
Cation exchange capacity ($meg.100g^{-1}$)	4.8
Carbonates (%)	32.2
Iron concentration ($mg.kg^{-1}$)	3584±200

Concentration of the Cu ($mg.kg^{-1}$)	300
pH before spiking	5.6
pH after spiking	6.2
Volume of conductive solution (ml)	2000
Time of experiments (h)	24
Dimensions of the electrokinetic cell (cm)	Height 9.2, Length 40, Width 15
Dimensions of the electrodes (cm)	Height 4.5, Length 6, Width 2
Electric field strength ($V.m^{-1}$)	74.1
Applied Voltage (V)	20

Electrokinetic cell was filled with 2000 ml of 10^{-2} M KNO_3. Addition of acetic acid or employing cation exchange membrane maintained the average pH of 2.5 in the anodic compartment and 12.5 in cathodic compartment. A power supply (Hewlett-Packard E3612A) was used to maintain 20V constant DC current and the current fluctuations were monitored (Fluke 12 multi-meter). Electrodes used in the remediation process were graphite plates or silver electroplated stainless steel electrodes supplied by Merck chemicals (Merck KGaA, Darmstadt, Germany). There were new electrodes used for each experiment therefore the surface area of electrodes remain constant in all the experiments. When several anodes were used for the remediation, they were interconnected through the 'banana' junction and attached to the power supply.

During the conducted experiments, sand samples were collected on a regular basis and taken for Cu analysis. In addition, at the end of each experiment, samples were collected from 3 points in the sand (Figure 3.1). After the sampling, sand samples were homogenized and total amounts of Cu was determined by air-acetylene atomic absorption spectrophotometry (Perkin-Elmer 300-AAS). The wavelength used for the determination was 324.8 nm, lamp current was 4 mA.

Sandy deposits with quartz intrusions were used for the experiments as a porous contaminated medium. The total humidity of sand at the beginning of experiments was 45% (determination by comparison to oven dried samples at 105^0C for 24 hours). After the electrokinetic experiments the humidity reached 90%, hence the samples were almost 100% immersed into the conductive solution. Samples were prepared for the morphological description and described according to Ribeiro (1998). For determination of particle size distribution sand was pretreated with peroxide to eliminate organics and with 20 ml solution of sodium hexametaphosphate with sodium carbonate (35.7 g of $(NaPO_3)_6$ + 7.49 g of Na_2CO_3 / one liter) for dispersion.

The textural classification was obtained by the triangular diagram according to Atterberg scale (Ribeiro, 1998). Cation exchange capacity (Ca, Mg, K and Na) was measured by saturation with ammonium acetate 1 M at pH 7, followed by distillation with NaOH 2M (Schollenberger and Simon, 1945).

The 'totals' of Cu were determined by HCl-HNO_3 extraction, aqua regia method (DIN 38414, 1983). Two or three ml of water + 7.5 ml of HCl (ρ = 1,19 g/l) + 2.5 ml HNO_3 (ρ = 1.4) was put into the flask where one gram of dried and crushed (to 75 µg) sand was placed and allowed to incubate for several hours at room temperature. Heated and maintained under the boiling conditions for 2 hours. 10 ml HNO_3 (c = 0.5 mol/l) was added and the sample was filtrated into a 100 ml flask and the residue washed with 20 ml HNO_3 c= 0.5 mol/l.

3. Results and Discussion

3.1. Relationship between the electrode spacing, electric field strength and the remediation time

Remediation time depends on the species transport rate and the spacing between opposite electrodes (Alshawabkeh et al., 1999). Hence when the distance between two opposite electrodes is increased, the remediation time increases significantly for the same number of mobile ions, porosity and tortuosity of the medium, and the same electric potential.

$$v = (n \times u \times \tau + ke) \times \Delta(-\phi) \tag{8}$$

where v is the velocity of species in the sand (m s^{-1})

n = porosity of the lake sand (dimensionless); u = mobility of the Cu ($m^2V^{-1}s^{-1}$); τ = sand tortuosity (dimensionless); ke = coefficient of electro-osmotic conductivity ($m^2V^{-1}s^{-1}$); $\Delta\phi$ = electric potential (V) .

If the distance between anode and cathode is r (m), then the time required for the Cu removal from artificially contaminated lake sand could be calculated as follows:

$$t = \frac{r}{v} \tag{9}$$

Despite relatively short sand spiking time, it was predicted that adsorption will take place at some extend. The velocity of Cu species was calculated using the following parameters: the porosity (n) and tortuosity (τ) in the lake sand were determined experimentally and were 0.51 and 0.3 respectively. The coefficient of electro-osmotic conductivity (ke) was 1.0×10^{-8} ($m^2V^{-1}s^{-1}$) and the electric potential ($\Delta\phi$) was 15.2 V.

The required remediation time was calculated for the current experimental conditions where r was 0.27 m (Table 3.1). Hence, in order to remove Cu from lake sand under given conditions, Equations (8) and (9) are solved using the parameter values stated above. Thus the theoretically determined time was 12 hours; however the laboratory experiments were conducted for 24 hours for the complete removal of the Cu from the contaminated matrix. In addition, theoretical considerations for different polarity electrode spacing are presented in Figure 3.2.

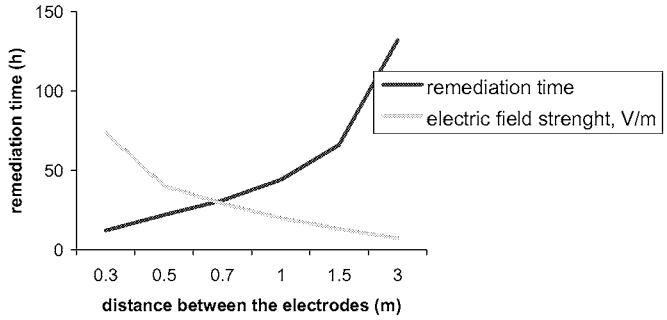

Figure 3.2. The relationship between the remediation time, the electric field strength and the electrode spacing

Additionally, the electric field strength for the given experimental conditions can be calculated as follows:

$$E = \frac{V}{r} \qquad (10)$$

where E = electric field strength (V m^{-1}); V is applied voltage (V) and r = distance between the oppositely charge electrodes (m).

According to Equation (10), when the distance between the electrodes was 0.27 m and the applied voltage was 20 V, the electric field strength was determined to be 74.1 $V.m^{-1}$. It is obvious that when the distance between the electrodes is increasing, the electric field strength is decreasing, while at the same time, the remediation time is increasing (Fig. 3.2). In order to decrease the remediation time and increase the electric field strength one needs to optimize the distance, number and the layout of the oppositely and the similarly charged electrodes.

3.2. The pH fluctuations in the anodic and cathodic compartments

If there are alkaline conditions in the sand, heavy metals, Cu in particular are likely to be adsorbed onto the negatively charged particles. Desorption of heavy metal contaminants from the sand surface by adjusting acidic conditions is essential in order to obtain high removal efficiencies (Broussous et. al., 2001; Bottino et al., 2001; Linkov and Belyakov, 2001).

It is apparent that when the membrane was involved in the experiments, the anions were prevented from penetrating into the anodic side and further into the sand and the pH was maintained acidic in the system. Cu species mobility is the highest under acidic conditions (Hansen et al., 1997; Probstein and Hicks, 1993; Pamukcu and Wittle, 1992; Hamed et al., 1991), it moves to the negatively charged cathode where precipitates in the alkaline environment as hydroxide and oxy-hydroxides.

3.3. Cu removal efficiencies

The layout of the electrode system, used in the laboratory scale experiments is schematized in Figure 3.3.

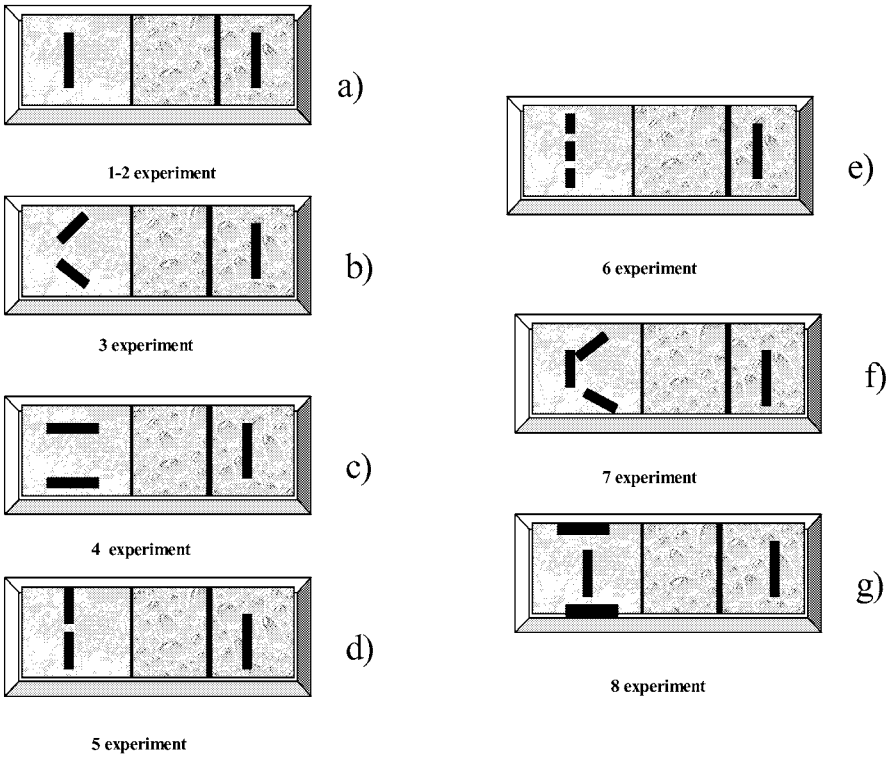

Figure 3.3. Electrode layout (view from above)

3.3.1. The one-anode system

The difference in the performance between silver and graphite electrodes was obvious (Table 3.2).

Table 3.2. Remediation efficiencies of the experiments

Experiments	Initial concentration ($mg.kg^{-1}$)	Removal efficiencies (%)
1 (silver anode)	300	31
2 (graphite anode)	300	86
3 (two graphite anodes)	300	91
4 (two graphite anodes)	300	80
5 (two graphite anodes)	300	91
6 (three graphite anodes)	300	82
7 (three graphite anodes)	300	78
8 (three graphite anodes)	300	78

The silver electrodes were consumed under the applied electric current, i.e. the anode in particular due to the acidic environment. Hence additional by-products were introduced into the sand. These by-products and also H^+, OH^- and NO_3^- ions consumed the electricity (Mattson et al., 200; Ho et al., 1997; Chen and Murdock, 1997) and were transported towards the electrodes according to their charges. The amount of silver ions found in the sand after the electrokinetic removal experiment was 220 mg kg^{-1} and additionally there were 85 mg kg^{-1} of silver deposited in the cathodic compartment. At the beginning of the experiment, no silver ions were detected in the sand or in the conducted solution. When the graphite electrodes were introduced, the Cu removal efficiency was significantly increased (Table 3.2).

3.3.2. The two-anode system

When the two anodes were arranged in such a way that they were inclined at the 45° angle and both were facing each other in the presence of a porous membrane, the amount of Cu in the sand after 12 hours of the experiment was almost ten times less than the initial concentration (Fig. 3.4b).

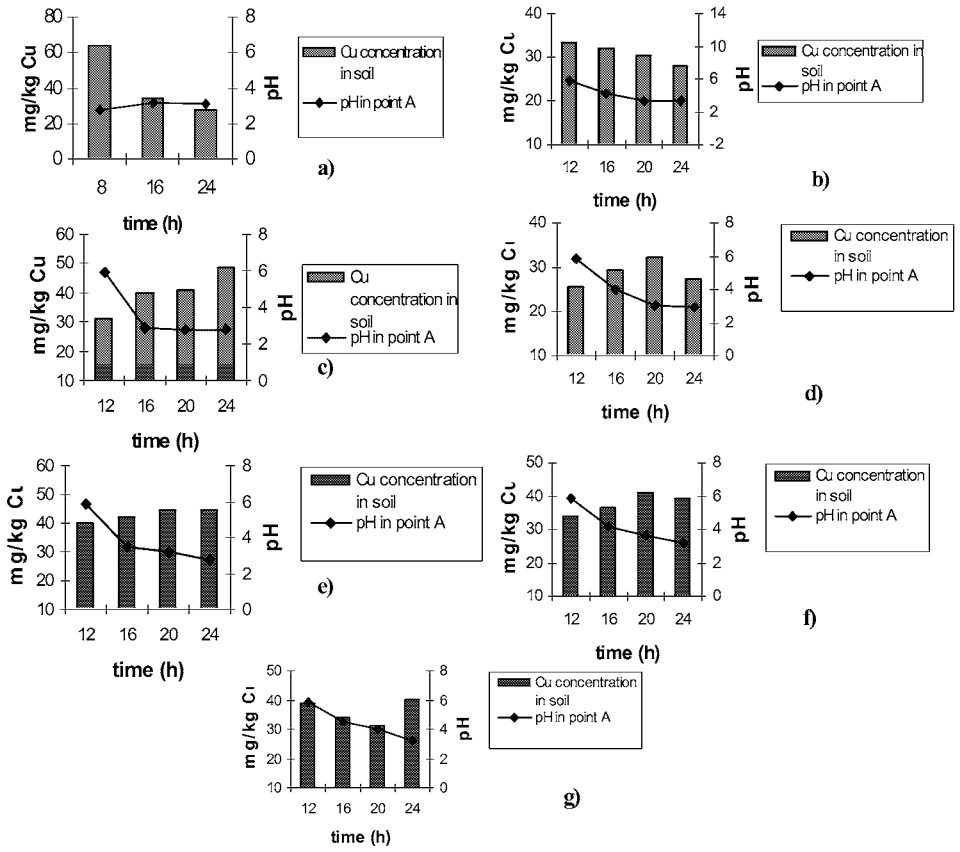

Figure 3.4. The pH and Cu concentration in the sand during experiments conducted with the employment of the membrane.

However, the concentration of Cu in the sand did not decrease significantly during the last 12 hours of the experiment, which may be due to the lack of the mobile fraction of ions (Chen and Murdoch, 1997) or the back diffusion of ions took place and the Cu returned to the sand. Thus, by using two anodes, the remediation process proceeded at a much faster rate than when one anode was used. Table 3.2 shows that with this electrode configuration, 91% removal efficiency may be achieved.

When two parallel anodes were introduced (Fig. 3.3c), the amount of Cu in the sand after 12 hours was about ten times less than the initial concentration (Fig. 3.4c). However, at the end of the experiment this amount almost doubled, indicating that part of already removed Cu returned into the sand. The geometry of electrodes may interfere with remediation process due to the conflict between the electric fields, i.e. the interference between the active and inactive electric fields (Alshawabkeh et. al., 1999). Furthermore, back diffusion of ions may also take place. Sah and Chen (1998) argued that diffusion starts to occur when sufficient amount of metal ions accumulate on the surface. Thus, after several hours of electrokinetic treatment, there is a significant amount of Cu ions present in the solution (data not shown). According to the law of entropy, ions start diffusing from high to low concentration areas, therefore there is an increase in Cu concentration in the sand (Fig. 3.3c).

Despite the considerably high removal efficiency (Table 3.2), this layout is not economically feasible if we compare it with the one-anode system. By using one anode system, 86% removal of Cu may be achieved, thus there is no significant economic advantage to be derived from using an additional electrode.

In the system with two linear anodes (Fig. 3d), the amount of Cu after approximately 12 hours in the sand was more than ten times lower level than the initial concentration (Figure 3.4d). The removal efficiency in this experiment was the highest of all the experiments conducted (Table 3.2). The reason for this is the large collective surface of electrodes.

3.3.3. The three-anode system

To investigate the effect of different electrode systems on Cu removal efficiencies, an experiment was conducted with linear anode system (Fig. 3.3e). After the first 12 hours, the amount of Cu retained in the sand was about 7 times less than the initial amount (Fig. 3.4e). However, later in the experiment, Cu ions partly migrated back to the soil.

When using three-triangle anode system (Fig. 3.3f), the amount of Cu left in the sand after the first 12 hours, was almost 9 times less than the initial level (Fig.3.4f). Nevertheless, during the last 12 hours some Cu migrated back to the soil. Despite the considerably high removal efficiency observed (Table 3.2), the experiment required several anodes, hence higher costs are required.

When two parallel and one perpendicular anode system (Fig. 3.3g) was applied, after the first 12 hour, it was possible to achieve almost 8 times lower amount of Cu retained in the soil than was present at the start of the experiment (Fig. 3.4g). However, later on in the experiment, the concentration of Cu increased gradually in the sand. The removal efficiency obtained using this particular layout is quite low in comparison to the two-anode system (Table 3.2), indicating that very large collective electrode surfaces may not be an efficient tool for the successful removal of contaminants from the media.

The reason for the lowest removal efficiency using three-anodes may be attributed to the effect of polarizations. During the electrolysis of water, H_2 and O_2 gases are constantly formed by each of the electrode and are attracted by the electrode surfaces. This gas 'film' together with other impurities increases the resistance that retards the reaction (Sah and Chen, 1998). Moreover, during the remediation process, there may be local Cu concentration gradients formed

in the sand around anodes. In order to overcome those gradients, voltage should also be increased, which also may also reduce the efficiency of electrokinetic remediation process.

4. Conclusions and future research trends

*Graphite electrodes are much more efficient than silver electrodes.

*Two-anode system (linear or triangular) is the most efficient system for removing Cu from contaminated lake sand. However, it is important to ensure the optimum conditions for the successful electrokinetic treatment of the contaminated media. It is necessary to calculate the distance between two or more electrodes, surface area and layout of electrodes and to optimize these parameters. In addition, it is also important to take into consideration 2D and 3D electrode layouts. Hence, future experiments should be focused on obtaining optimum electrode surface area, which is cost efficient, easy to implement and presents the highest removal efficiencies of contaminants from chosen media.

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CHAPTER 4: COPPER AND CHROMIUM ELECTROKINETIC MIGRATION IN CCA-TREATED TIMBER WASTE

Jurate Virkutyte[1]*, Emiliya Velizarova[2], Alexandra B. Ribeiro[2] and Mika Sillanpää[1]

[1]Department of Environmental Sciences, University of Kuopio, 181 FIN-50101, Mikkeli, Finland
[2]Departameto de Ciencias e Engenharia do Ambiente, Facultade de Ciencias e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal
* The corresponding author [Email: jurate.virkutyte@uku.fi, tel. +358153556201, fax: +358153556365]

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Abstract

Chromated copper arsenate (CCA) – treated timber waste is hazardous for the environment due to the leakage of copper, chromium as well as arsenic to the soil and the groundwater. During many years main waste handling techniques were incineration and landfilling. However, in the last few decades, new emerging alternatives appeared. The study concentrates on electrodialytic removal of copper and chromium and their migration behavior in the wood chips and sawdust matrix in an applied electric field. The method is based on the movement of the charged particles in the electric field, enhanced by incubation with oxalic acid (2.5% w/w) and various placement of the contaminated waste in the electrodialytic cell area to analyze the distribution of chemicals in the proposed matrix. The validation of the proposed method was tested in three experiments where CCA contaminated wood chips and clean sawdust were placed in various places of the cell, i.e. adjacent to the cathode and anode compartments and in the mid-section of the cell. The duration of each experiment was 14 days and the current was kept constant at 40 mA. The migration patterns obtained differ in all three experiments due to the electromigration phenomenon as well as formed complexes. There were no attempts demonstrated to assess the efficiency of electroosmotic phenomenon. To predict the formation of copper and chromium species at certain pH and Eh, the computer modeling program MTDATA to generate Pourbaix diagrams was used.

Keywords: CCA-treated timber waste, heavy metals, electrodialytic migration

1. Introduction

Wood treatment with chromated copper arsenate (CCA) preservatives has been used in order to increase the life expectancy of the wood, but at the same time it may cause heavy metal contamination of the environment. Misuse of these chemicals can be potentially hazardous to humans and other forms of life (Bhattacharya et al., 2002; Hingston et. al., 2001; Bjorklund et. al., 1998; Jacks and Bhattacharya, 1998).

In order to assess possible heavy metal treatment alternatives, the electrokinetic migration of CCA chemicals from the contaminated chips through the clean sawdust to the anode or cathode compartment was investigated. The main purpose of the current study was to expand the already existing though scarce knowledge about the migration of copper and chromium in the contaminated wood chips under the applied electric field and the possible advantages of the contaminants placement in the electrodialytic remediation equipment for the overall heavy metal removal process efficiency. To predict the formation of copper and chromium species at certain pH and Eh, the computer-modeling program MTDATA to generate Pourbaix diagrams was used.

2. Materials and Methods

Laboratory scale experiments of 14 days each were conducted in duplicates with wood chips and sawdust. The chips were prepared from an out-of-service CCA-treated *Pinus pinaster* Ait. Pole (Leiria, Portugal). The treatment scheme as well as the CCA formulation is unknown. Clean sawdust from a similar species was also prepared. Total amount of Cu and Cr was determined according to British Standard 5666 Part 3 (BS 5666, 1986). Chips and sawdust weights presented in the result and discussion section are dry weights. Table 4.1 presents experimental conditions of the experiments.

Table 4.1. Experimental conditions (according to Velizarova et al., 2004; Ribeiro et al., 2000)

Parameter	Value
Initial Cu concentration ($mg.kg^{-1}$)	3149±114
Initial Cr concentration ($mg.kg^{-1}$)	8281±420
Initial As concentration ($mg.kg^{-1}$)	8111±871
Intial pH of chips	5.6
Dimensions of wood chips (mm)	length 10–15, width 2–10, thickness ~1 mm
Fine powder fraction of chips	10%

All experiments were conducted in the electrodialytic cell (Fig. 4.1) developed at the Technical University of Denmark (Ottosen et al., 1992). Electrodialytic cell consists of three compartments, i.e. anode, cathode and a central one where contaminated chips and sawdust are placed. The anode compartment consisted of anode, anolyte and anion exchange membrane, whereas the cathode compartment – cathode, catholyte and cation exchange membrane. The layout of three experiments is presented in the Figure 4.2.

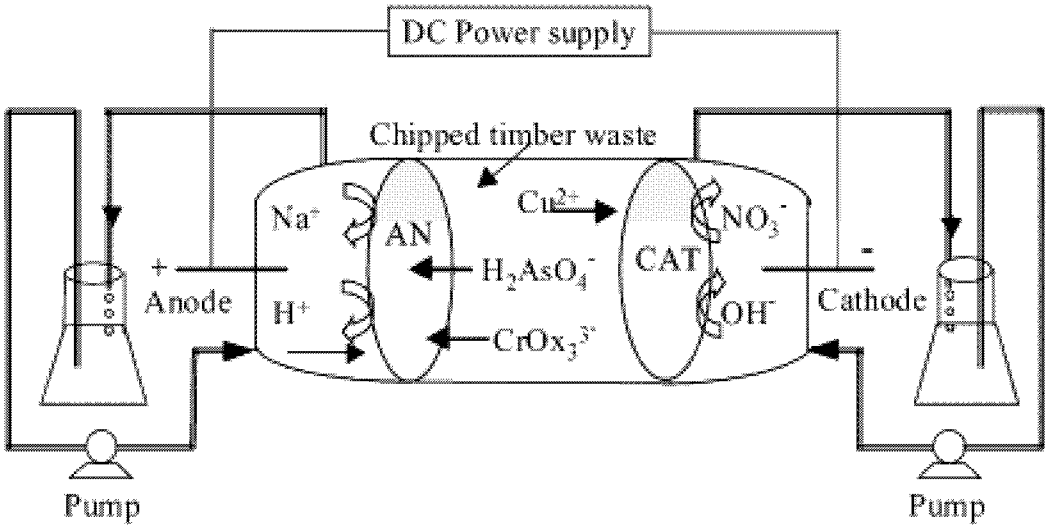

Figure 4.1. Electrodialytic cell, DTU concept (according to Ribeiro et al., 2000)

The central compartment, anode as well as cathode compartments were separated by anion-exchange and cation-exchange membranes (AN): IA1-204SXZL386; (CAT): IC1-61CZL386, both from Ionics Inc, USA) as schematized in Figure 1. 1000 ml of 10^{-2} M $NaNO_3$ was placed in the anode and cathode compartments respectively. The average pH of 2 was maintained in the catholyte by periodic adding of concentrated HNO_3.

In addition, pumps were used to re-circulate electrolytes. A power supply (Hewlett-Packard E3612A) was used to maintain 40mA constant DC current and the voltage fluctuations were

monitored (Fluke 37 multimeter). The electrodes used in the remediation process were platinized titanium bars with a diameter of 3 mm and a length of 5 cm (Bergsøe Anti Corrosion A/S, Denmark).

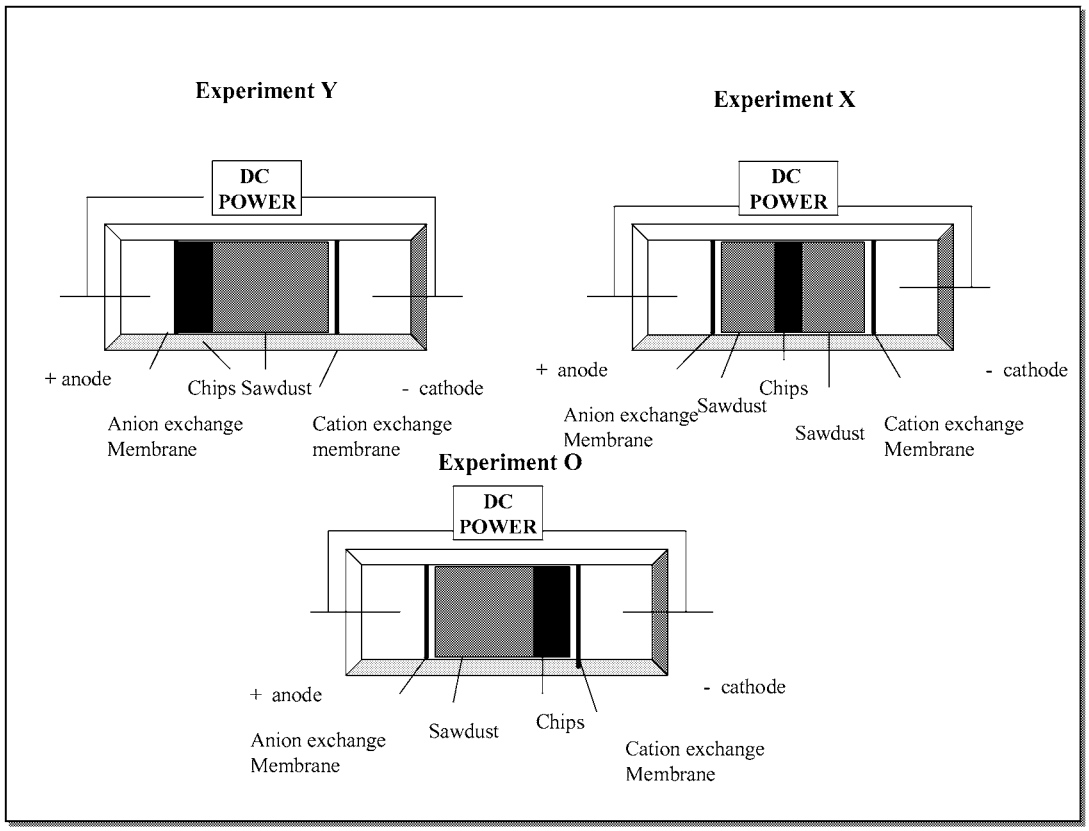

Figure 4.2. Placement of contaminated chips.

Under the applied low-level direct current, ions moved in the electric field but the anion-exchange membrane prevented cations from reaching the chips or sawdust. At the same time, cation-exchange membrane prevented anions from penetrating into the contaminated chips area and clean sawdust (Figure 4.1). To prevent the OH^- ions formed at the cathode due to the electrolysis of water from interfering with the remediation process, HNO_3 was introduced into the cathode compartment to keep the pH at 2 – 3.

To induce the movement of contaminants from the chips, incubation with 2.5% (w/w) oxalic acid was used beforehand. Incubation of contaminated chips as well as sawdust was maintained for 36 hours. After the incubation period was over, chips and sawdust were placed into the remediation cell. During the experiments, anolyte and catholyte samples were collected and taken for analysis for Cu and Cr. In addition, at the end of each experiment, chips and sawdust,

i.e. the amount of matrix in the central compartment was sliced into five slices and the total amounts of Cu and Cr were obtained in accordance to the British Standard 5666 Part 3 (BS 5666, 1986). Both Cu and Cr were determined by atomic absorption spectrophotometry (Perkin-Elmer 300-AAS).

The pH of the sand slices was measured as reported by Ottosen et al. (1997). 10 g of wood chips and 50 ml of distilled water were mixed for 1 h and pH was measured using Metrohm electrode (glass electrode 602, Metrohm, Switzerland).

3. Results and Discussion

3.1. Copper and chromium species distribution under the electric potential and pH

A potential-pH equilibrium diagram shows that under acidic conditions, Cu mainly present as positively charged ions, which are predicted to migrate towards the cathode (Fig. 4.3a). Furthermore, chromium speciation mostly depends on the redox conditions, e.g. when strong reducing and oxidizing conditions prevail, chromium forms anionic complexes, but under slightly reducing conditions, positive Cr ions are formed (Fig. 4.3b). However, the diagram describes an ideal system and does not take into the consideration possible dissolution and precipitation processes (Velizarova et al., 2002).

When the CCA-treated timber waste in placed with oxalic acid, oxalates or other compounds are formed. According to the thermo-chemical species distribution (Davies et al., 2002), the major species of copper in acidic medium (pH < 6.5) are Cu_2Ox^{2-}, and $CuOx^{2-}$ (Fig. 4.3a). In addition, when the oxidizing conditions prevail, Cu^{2+} and Cu^{+} also exist. However, when the pH in the electrokinetic cell increases (pH 5 – 12.5), in the reducing environments, CuO and free Ox^{2-} are the major species. At the higher Eh, copper hydroxide complexes and CO_2 are present (Fig.4.3a).

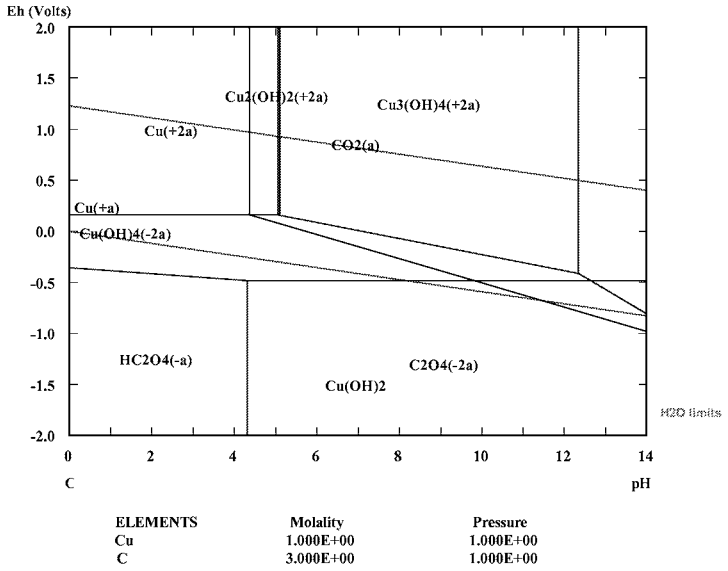

Figure 4.3a. Thermo-chemical copper species distribution

When the pH is maintained acidic and at the reducing environment (low Eh), major chromium species are Cr (III) hydroxides and Cr^{3+} ions (Fig. 4.3b). In oxidizing environments, the predicted chromium species are $Cr_2O_7^{2-}$. When the pH is 6 – 12.5, CrO_4^{2-} and free Ox^{2-} exist (Fig. 4.3b).

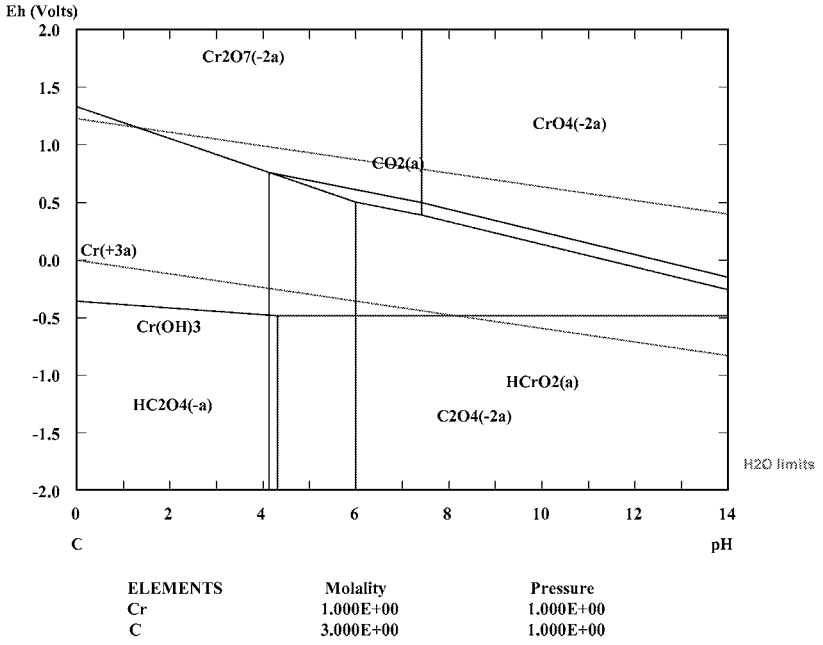

Figure 4.3b. Thermochemical chromium species distribution

Figure 4.4 presents the computer simulated oxalate formation.

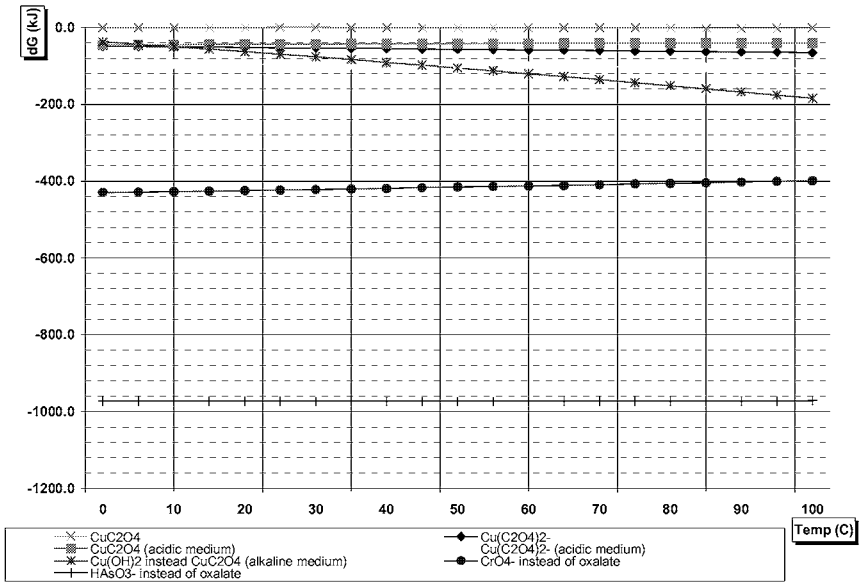

Figure 4.4. Oxalate formation.

3.2. Effect of electricity on copper migration

There was an induced movement of copper compounds in all three experiments. In addition, the predominant direction of those compounds was always towards the anolyte solution reaching 40 mg L^{-1} at the maximum (Fig. 4.5a).

The movement of copper towards the catholyte was negligible in all three experiments (Fig. 4.5b, d, f). Additionally, during the experiment Y there was significant penetration of copper through the anion-exchange membrane to the anolyte. This may be explained as the availability of negatively charged copper species. Indeed, Clausen, (2004) also observed a formation of negatively charged copper species during the remediation of CCA-treated timber waste. Also, copper ions may have also been transported via the ion flux from the contaminated chips area due to the particular placement of the chips in the electrodialytic cell.

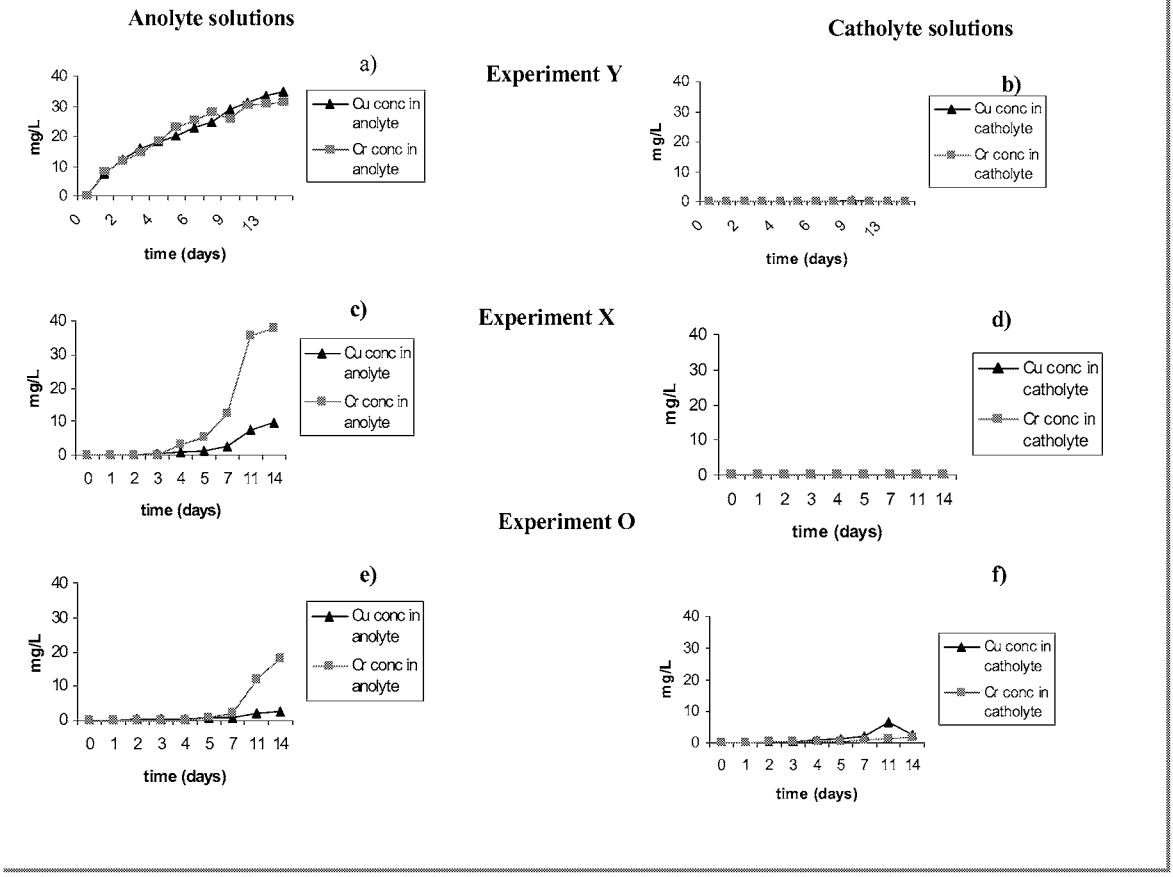

Figure 4.5. Copper and chromium concentration in the anodic and cathodic solutions.

It is likely to believe that the main anionic complex formed after the incubation with oxalic acid was $CuOx_2^{2-}$ (Clausen, 2004), which migrates towards the positively charged anode. Despite the movement of negatively charged compounds, Figure 4.5a suggests that the insoluble CuOx (copper oxalate) prevails (Hingston et al., 2001) and it remains bound to the wooden chips matrix and therefore impairs the copper migration process.

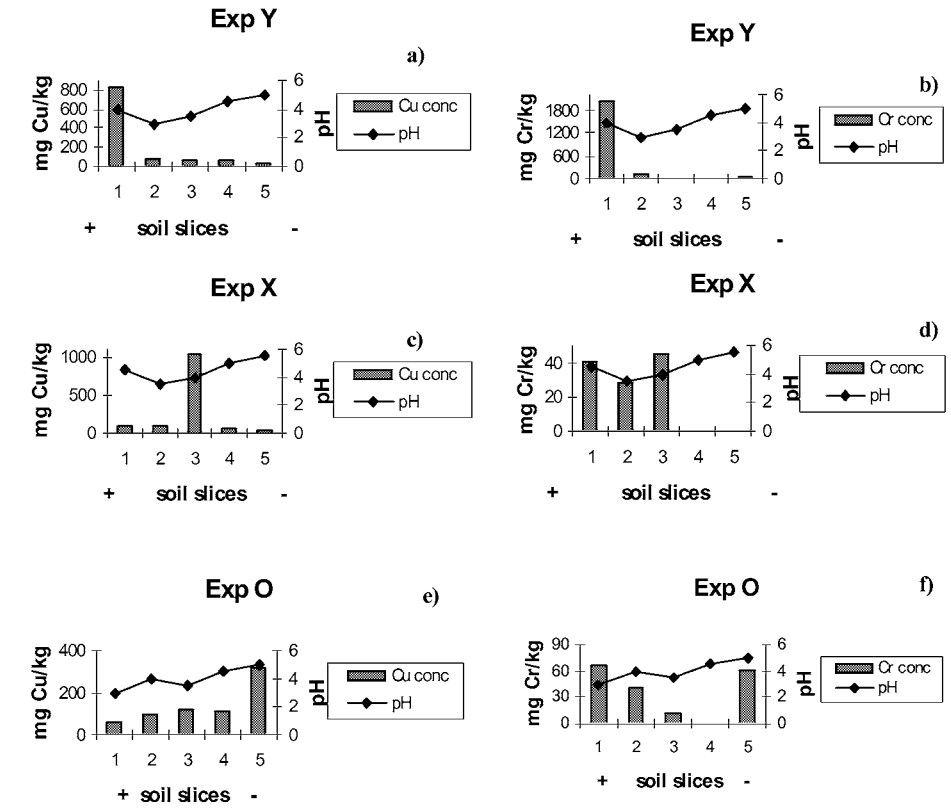

Figure 4.6. Copper and chromium migration and the pH distribution in the matrix at the end of experiments Y, X and O respectively

Experiment X shows similar copper migration as the experiment Y. It is obvious (Fig. 4.5c) that chips incubation process with oxalic acid produces copper oxalate with limited water solubility, which remains in the wood matrix, therefore the migration of copper ions is limited (Velizarova et al., 2002). Significant amount of copper ions move as the negatively charged complex (Fig. 4.5c). In addition, copper deposited onto the cathode is more than ten times the copper deposited onto the anode. It suggests that after the free oxalic acid in the sawdust is no longer available, copper moves as a free cation (Cu^{2+} or Cu^{+}) towards the cathode (Ribeiro et al., 2000).

Results obtained for the experiment O show different copper compounds migration pattern than it was during the experiments Y and X. Figure 4.5e shows that there is only minor amount of copper compounds in the anolyte solution at the end of the experiment. Additionally, a significant amount of copper was precipitated onto the cathode and in the cation-exchange membrane. This process may be explained by the movement of the charged particles (Virkutyte et al., 2002; Acar et al., 1993). In other works it was established that part of the copper compounds, under similar experimental conditions, is bound to the chips as insoluble oxalates, a part existing as negative complexes and the rest existing as free copper cations (Ribeiro, 1998; Ribeiro et al., 2000).

After the application of the direct current, copper ions and complexes as well as a free oxalic acid begin to migrate towards the electrodes. As oxalic acid bears negative charge, it migrates towards the positive anode. The ionic flux involves negatively charged copper complexes, which moves from the cathode compartment (Fig. 4.6e) to anode side. Copper behavior in the experiment O could be explained by the existing pH conditions close to the cathode side (pH 12.5), which are favorable for the hydroxide formation (CuOH and $Cu(OH)_2$) and subsequent copper precipitation (Alloway, 1995). However, high concentration free copper ions are very close to the cathode compartment and they move together with the flux of water according to their charge to the cathode, i.e. from the high concentration to the low concentration area and precipitate in the cation-exchange membrane and onto the electrode.

3.3. Effect of electricity on chromium migration

In all experiments, chromium forms negative Cr (VI) complexes with oxalic acid ad moves towards the anode. Hence, when the pH in the cathode compartment is significantly reduced (to the final pH of 2.5), chromium is also reduced to Cr (III) and moves towards the cathode as a positively charged complex or as Cr^{3+} (Velizarova et. al., 2002; Vallejo et al., 2001; Hingston et al., 2001). In addition, notable amount of chromium remains in the chips (Fig. 4.6b, d, e).

Experiment X presents similar chromium migration profile in comparison to the experiment Y. Significant amount of chromium precipitates in the anion exchange membrane and is found in the anolyte at the end of the experiment. As it is reported that Cr (VI) forms soluble and mobile chromium complexes like $Cr_2O_7^{2-}$, $HCrO_4^-$ or CrO_4^{2-} (Kartal, 2003; Stephan et al., 1996). Hence, under particular conditions, those compounds move to the positively charged anode. In addition, the possibility of the formation of $CrOx_3^{3-}$ also cannot be excluded. Formed negative complexes migrate to the anode compartment and precipitate in the anion-exchange membrane (Fig. 4.6d). However, some chromium precipitates in the cation-exchange membrane, which indicates the existence of the positive Cr (III) complexes (Clausen, 2004; Vallejo et al., 2000) or free Cr^{3+} ions.

Experiments O presents the similar results to the experiment Y and X, however there are some slight difference observed. The highest amount of chromium is found precipitated in the anion-exchange membrane and also a significant amount of chromium moved to the anode precipitating either in the sawdust or in the anolyte solution (Fig. 4.6f). It indicates that the negative chromium complexes prevail in this particular experiment. However, as it is presented in figure 4.5f, chromium either remains bound to the wood chips or moves to the cathode or precipitates in the cation-exchange membrane or catholyte. It is possible to assume that ionic flux dominate towards the cathode and Cr (III) positive complexes (Hingston et al., 2001) or Cr^{3+} or $Cr(OH)^{2+}$ exist.

3.4. Effect of pH on oxalate complexes

It has been reported by Mytich et al (2005) that chromium has a strong tendency to bind oxygen containing functional groups and form complexes with organic ligands, including oxalate, citrate, malonate, EDTA and DTPA, which are soluble and stable within environmental pH range. However, according to the speciation program, chromium tends to form CrO_4^- more than oxalates (Fig. 4.4). Moreover, Venkateswarlu et al. (2005) also determined that despite chromium forms strong complexes with oxalate, when the pH is 2.5 - 3, chromium does not form the complex due to its slow kinetics.

There was a significant different found in Cu and Cr concentrations in the wood chips between Exp Y and Exp X and O. According to Figure 4.6a and b, there were almost none

positive Cu and Cr species formed during the electrodialytic experiment. Ribeiro et al. (2000) reported that a reduction of, for example chromate by oxalate, is possible at acidic conditions. Thus, when strong acidic conditions prevail (as in this case pH 2.5 at the anode), positive Cu and Cr compounds are not formed and most of the contaminants either remain bound to the chips matrix or are transported to the anode as anions. Similar results were obtained by Velizarova et al. (2004) where it was observed dominant anionic fluxes to the anode compartment when negatively charged complexes between metal cations and oxalic acid were formed.

4. Conclusion and further research trends

* Oxalic acid induces and enhances the migration of the contaminants in the electric field; however, the complex formation chemistry needs to be further investigated.

* If placed adjacent to the anode compartment, copper as well as chromium mostly moves to the anode side via the formation of negatively charged species.

* If the contamination area is in the mid-section of the cell, contaminants either remains in the area bound to the wooden matrix or move to the electrodes as if they were free ions.

* If the contamination area is close to the cathode, contaminants either act as if they were positive ions or act according to their regular charges, i.e. copper moves as a positive free ion and chromium moves as negatively charged ion.

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CHAPTER 5: CU AND TRACE ELEMENTS FRACTIONATION IN ELECTROKINETICALLY TREATED ANAEROBIC GRANULAR SLUDGE

Virkutyte, J.[1,2], van Hullebusch E.[1], Sillanpää, M.[2] and Lens, P.[1] *

[1] Sub-department of the Environmental Technology, University of Wageningen, 'Biotechnion' - Bomenweg 2, PO Box 8129, 6700 EV Wageningen, The Netherlands.
[2] University of Kuopio, Department of Environmental Sciences, Laboratory of Applied Environmental Chemistry, PO Box 181, 50101 Mikkeli, Finland
*The corresponding author [email: piet.lens@wur.nl, tel. +31 317483339, fax: +31 317482108].

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Abstract

The effectiveness of electrokinetic treatment on metal fractionation and fractions transport in electric field in anaerobic granular sludge from an UASB (up-flow anaerobic sludge-bed) reactor artificially contaminated with Cu and was studied. The contaminant $Cu(NO_3)_2$ was supplied to the granular sludge to reach an initial Cu concentration of 1150±50 $mg.kg^{-1}$ wet sludge. This study evaluated the variations in Cu fractionation after electrokinetic treatment at 0.15 $mA.cm^{-2}$ under different conditions, i.e., anolyte pH (2.5 – 12.5), complexation with $EDTA^{4-}$ or pre-incubation (30 days incubation with Cu). Pre-incubation of sludge with Cu was performed to compare the changes in fractionation with changes occurred in fresh anaerobic granular sludge fractions. The migration in the applied electric field strongly depended on the fractionation in the sludge. Acidification of the sludge (final pH 4.2 in the sludge bed) with the intention to desorb the Cu species bound to the residual fraction did not result in an increased mobility, despite that a higher quantity of Cu was measured in the more mobile fraction (i.e. exchangeable / carbonate fractions) at final pH 4.2 compared to circum-neutral pH conditions. The addition of the strong chelating agent $EDTA^{4-}$ (molar ratio Cu^{2+}:$EDTA^{4-}$ of 1.2:1) did not enhance the mobility of Cu from the organic / sulfides and residual fractions, despite that it induced a reduction of the total Cu content of the sludge. It was observed that the presence of sulfide precipitates influences very likely the Cu mobilization from these less mobile fractions (residual fraction and to a lesser extend the organic/sulfides fraction).

Keywords: fractionation, Cu, electrical treatment, granular sludge.

1. Introduction

The electrokinetic remediation technique is widely used to separate and extract charged contaminants from soils (Hamed et al., 1991; Acar and Alshawabkeh, 1993; Van Cauwenberghe, 1997; Yeung et al., 1997, Maini et al., 2000), sludge (Zagury et al., 1999; Kim et al., 2002; Jakobsen et al., 2004) or timber waste (Velizarova et al., 2002) by employing a low-level direct current in the range of several $mA.cm^{-2}$. The low-level current induces the mobility and results in solubility of heavy metals due to electromigration and electroosmosis flow (Hamed et al., 1991; Acar and Alshawabkeh, 1993; Mattson and Lindgren, 1995; Virkutyte et al., 2002; Kim et al., 2002).

While there is a vast amount of data about the application of electrokinetic treatments to remove heavy metals from contaminated matrices, there is a lack of information on the characteristics of the electrokinetically treated sludges such as the fractionation of heavy metals.

Cu and trace elements are essential elements but are potentially toxic at high concentrations and may produce deficiency symptoms at very low concentration in the environment (Shrivastava and Banerjee, 1998). Heavy metals occur in sludges in various physico-chemical forms, such as, soluble, adsorbed, exchangeable, precipitated, organically complexed and residual phases (Hayes and Theis, 1978; Angelidis and Gibbs, 1989). Analytical limitations, which are imposed by selectivity and interference, do not allow a complete differentiation of metals between physicochemical forms in the sludge matrix (Hsiau and Lo, 1998). However, the chemical Cu, macro and trace element fractionation in the solid matrix of sludges can be determined by for instance using the revised BCR sequential extraction scheme, as proposed by Mossop and Davidson (2003).

Sequential extraction procedures have been developed predominantly to determine the amounts and partitioning of metals present within soils or sediments samples, sewage sludge and sludge treated soils (see Filgueiras et al., 2002 for review). Fractionation procedures are often criticized because of their complexity and difficulty in interpretation, arising from potential problems such as lack of specificity of extractants and re-adsorption of metals during extraction. Nevertheless, providing that such limitations are recognized, sequential fractionations can provide extremely useful information on metal distribution in sludges, particularly for comparative purposes (McLaren and Clucas, 2001).

Kim et al. (2002) observed that metals present in exchangeable/carbonates and organic/sulfides fractions are the most available to plants and biota. Therefore, the fractionation studies may assist in determination of the potentially harmful effects of contaminated sludge if it is applied to the environment. In the present study, mesophilic anaerobic granular sludge was chosen as a model for the experimental medium. To estimate the potential environmental impacts of metals present in the sludge the sequential and *aqua regia* extraction were applied. The changes in the Cu fractionation after different electrokinetic treatment strategies (i.e., exposure to different pH values, complexation with EDTA, pre-incubation) of artificially Cu contaminated sludge granules were evaluated. The effect of the electricity on the fractionation of macro and trace elements in the sludge cake were also investigated.

2. Materials and Methods

2.1. Electrokinetic set-up

A 'closed' laboratory-scale electrokinetic cell was used in this study as described by Ottosen and Hansen (1992). The cell consisted of a cylindrical glass container (diameter 20 cm, length 26 cm) with a distance between the electrodes of 17 cm. In the electrokinetic cell (Fig. 5.1), the central compartment from the anode and cathode compartments was separated by, respectively, anion-exchange (IA1-204SXZL386) and cation-exchange (IC1-61CZL386) membranes (Ionics Inc, Watertown, Massachusetts, USA). The anode and cathode were immersed into a 0.05 M KNO_3 conductive solution (Fig. 5.1). The electrodes (diameter 3 mm, length 5 cm) were titan bars (supplied by Elektronika-WUR, the Netherlands).

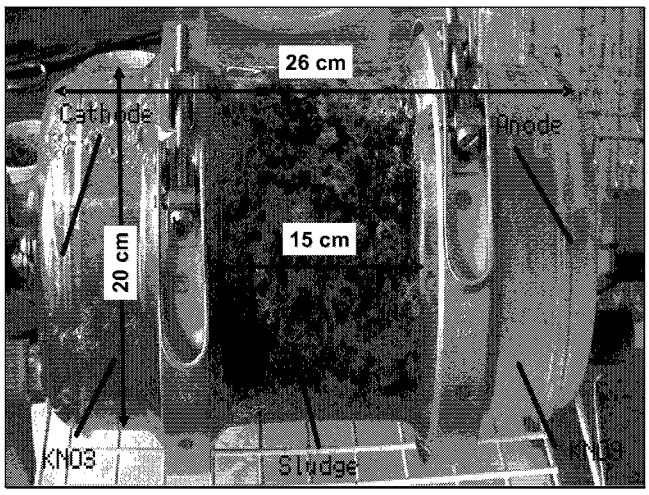

Figure 5.1. The'closed' electrokinetic cell.

In the electrokinetic cell, a power supply (Hewlett-Packard 613 Altai, Germany) was used to constantly maintain a 0.15 $mA.cm^{-2}$ DC current. The voltage fluctuations were monitored with a Fluke 112 multimeter (Fluke, Eindhoven, The Netherlands).

Peristaltic pumps (Marlow 502S) allowed a recirculation of the electrolyte solutions. The average flow rate in the electrolytes was maintained at 5 $ml.min^{-1}$.

2.2. Source of biomass

Anaerobic granular sludge was obtained from a full-scale upflow anaerobic sludge-bed (UASB) reactor (Industriewater Eerbeek B.V., Eerbeek, the Netherlands) treating paper-mill wastewater (Lens et al., 1999). This particular sludge was chosen as a sample porous medium containing high sulfide concentrations and relatively high amount of heavy metals, which are important for the growth or, in high concentrations, may be detrimental for the microorganisms. Total suspended solids (TSS) is a measure of the mass of fine inorganic particles suspended in the water. Volatile Suspended Solids (VSS) are those solids lost on ignition (heating to 550°C.) They give a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge and industrial wastes. The main sludge characteristics are presented in Table 5.1.

Table 5. 1. Main characteristics of anaerobic granular sludge (Hullebusch et al., 2005; Osuna et al., 2004).

Characteristics	Amounts
Mean density	1040 $kg.m^{-3}$
Ash content	25%
Total Suspended Solids (TSS)	22% (±0.2%)
Volatile Suspended Solids (VSS)	73.9% (±0.2%)
Carbonates (% of TSS)	0.4±0.2
Total sulfur	41.8±1.0 $mg.g^{-1}$ TSS
Background Cu concentration	150±20 $mg.kg^{-1}$ TSS
Initial Cu concentration	1150±50 $mg.kg^{-1}$ TSS
Initial pH	7.1

The UASB concept was born out of the recognition that inert support material for biomass attachment was not necessary to retain high levels of active sludge in the reactor. Instead the UASB concept relies on high levels of biomass retention through the formation of sludge granules. Anaerobic granular sludge bed technology refers to a special kind of reactor concept for the "high rate" anaerobic treatment of wastewater (Lettinga et al., 1980). Methanogenic microbial consortia in UASB sludges convert organic compounds to methane under anaerobic conditions (Ahn et al., 2002). Sludge granules are developed by self-granulation of microorganisms and dynamic balance between granule growth and decay results in coexistence of UASB sludges with different sizes in the reactor.

2.3. Experimental design

The amount of sludge placed in the electrokinetic cell was 1000 g (wet sludge). It was artificially contaminated with 3.78 g of $Cu(NO_3)_2$, which gives 1000 $mg.kg^{-1}$ (wet sludge) of Cu. Thus, the initial Cu concentration due to the background Cu concentration was 1150±50 $mg.kg^{-1}$ TSS. The contamination procedure was as follows: 1000 g of anaerobic granular sludge amended with the specific $Cu(NO_3)_2$ and $EDTA^{4-}$ concentration was placed into a closed plastic container for 48 hours (Reddy et al., 1997). The content of the plastic container was frequently and thoroughly mixed. After the contamination procedure was over, this sludge, still suspended in the Cu ($EDTA^{4-}$) containing supernatant, was mounted in the electrokinetic set-up. In the $EDTA^{4-}$ amended experiments, 3.78 g of Na_2H_2EDTA was added simultaneously with $Cu(NO_3)_2$ (molar ratio of Cu^{2+} : Na_2H_2EDTA at 1.2:1) for the freshly spiked sludge. When testing the effect of sludge pre-incubation, the sludge was incubated in an anaerobic chamber with 3.78 g of $Cu(NO_3)_2$ for 30 days (including 48 hours), and supplemented with 3.78 g of $EDTA^{4-}$. The pre-incubation of sludge with Cu was performed to compare the changes in fractionation with changes, occurring in fresh anaerobic granular sludge fractions when low level direct current was applied. Anaerobic conditions were maintained during the incubation procedure to avoid the COD conversion to additional sludge biomass, oxidation of sulfides to sulfates and lethal effects of oxygen to sludge microorganisms.

The experimental layout was a closed system and hence no Cu, trace and macro elements escaped from the electrokinetic cell. Therefore no mass conservation was checked as it is assumed that heavy metals remain in the matrix or adsorb to the membrane. Table 5.2 shows experimental conditions of the experiments.

Table 5. 2. Main experimental characteristics.

Exp	Duration (days)	Current (mA)	Current density ($mA.cm^{-2}$)	Sludge length (cm)	average pH in sludge cake	Contam.	Sludge
A	14	40	0.15	15	7.7	$Cu(NO_3)_2$	Fresh
B	14	40	0.15	15	7.7	$Cu(NO_3)_2$	Pre-incubated
C	14	40	0.15	15	4.2	$Cu(NO_3)_2$	Fresh
D	14	40	0.15	15	4.2	$Cu(NO_3)_2$	Pre-incubated
A'	14	40	0.15	15	7.7	CuEDTA	Fresh
B'	14	40	0.15	15	7.7	CuEDTA	Pre-incubated
C'	14	40	0.15	15	4.2	CuEDTA	Fresh
D'	14	40	0.15	15	4.2	CuEDTA	Pre-incubated

The sludge was put in the electrokinetic cell for 14 days in all experiments. This period was chosen because after 10 days, the voltage had increased significantly (up to 90 V) and remained constant for at least 2 days and then decreased down to 10V. The low voltage indicates that the entire acidic front had passed through the sludge cake. After the electrokinetic treatment, the sludge cake was split into three portions, i.e. a portion close to the anode, a portion close to the cathode and a mid portion between them. Each portion was homogeneously mixed before analysis. The electro-osmotic flow was not quantified in the experiments due to the absence of outflow from the cathode.

The initial pH of the sludge cake was 6.9. However when spiking solution with the pH of 7.2 was applied to the sludge cake, the pH reached 7.1. When the pH fluctuations were uncontrolled in the electrolytes, it was 12.5 in the catholyte and 2.5 in the anolyte. This gave a final pH of 7.5 - 7.8 in the sludge cake upon termination of the electrokinetic treatment. When

the pH in the catholyte was set to 2.5 by 1 M HNO_3 addition, the pH in the sludge cake was 4.0 - 4.3 upon termination of the electrokinetic treatment.

2.4. Analytical techniques

2.4.1. Pseudo-total metal analysis

The pseudo-total metal content (expressed as mg metal kg^{-1} TSS) of sludge was determined by digestion with the *aqua regia* procedure (Florian et al., 1998). For metal determination, 0.5 g TSS of anaerobic granular sludge were treated with 10 ml of *aqua regia* in TEFLON® PFA (PerFluoroAlkoxy resin) digestion vessels, in a temperature controlled microwave oven Milestone ETHOS E (Milestone Inc; Monroe, CT). The sample volume was completed to 100 ml with ultra pure water. After digestion, the concentrations of total metals were analysed using an Atomic Absorption Spectroscopy (AAS) flame (Perkin-Elmer 300) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP – OES; Varian MPX CCD, Vista Australia). The following wavelengths were used: 228.802, 213.598, 259.940, 216.555, 202.548, 422.673 and 279.553 nm for Co, Cu, Fe, Ni, Zn, Ca and Mg, respectively for ICP-OES measurements.

2.4.2. Revised sequential extraction (BCR) scheme

The revised BCR scheme is designed based on an acetic acid extraction of approximately 1 g TSS of granular sludge (step 1), hydroxylamine hydrochloride extraction (step 2) and hydrogen peroxide oxidation and ammonium acetate extraction (step 3) as described by Mossop and Davidson (2003). To extract the residual phase (step 4), a mixture of 2.5 ml HNO_3 (65%) and 7.5 ml HCl (37%) (*Aqua regia* digestion) was added to the residue and the filter from fraction 3. After microwave destruction, the samples of step 4 were paper filtered and diluted to 100 ml with ultra pure water. Compared to the original BCR procedure, the revised protocol involves the use of an increased concentration of $NH_2OH{\cdot}HCl$ and lower pH as described by Mossop and Davidson (van Hullebusch et al., 2005). The chemicals used for the extraction are presented in Table 5.3.

Table 5.3. The chemicals used for the sequential extraction to determine the Cu speciation in the sludge fractions after the electrokinetic experiment

Fraction	Extracting agent	Extraction conditions	
		Shaking Time[1]	Temp
1. Exchangeable + carbonate	40 mL CH_3COOH (0.11 M, pH = 7)	16 hours	20°C
2. Fe and manganese oxides	40 mL NH_2OH-HCl (0,1 M, pH=1.5)	16 hours	20°C
3. Organic Matter and sulfides	20 mL H_2O_2 (30% pH = 2) and then	1 hour 2 hours	20°C 85°C
	40 mL CH_3COONH_4 (1 M, pH = 2)	16 hours	20°C
4. Residual	10 mL demineralised water and 10 mL Aqua regia (HCl/HNO_3, 3:1)	26 min.	Microwave-oven[2]

[1] Shaking was applied at 30 rpm
[2] Extraction of the residual fraction in the microwave was equal with the pseudo-total extraction method

These extractions are associated to the exchangeable/carbonate (bound to carbonate, step 1), oxides phase (bound to Fe and manganese oxides, step 2) and the organic/sulfides phase (bound to organic matter/sulfides, step 3).

2.4.3. Evaluation of analytical performance

The analytical performance of the laboratory procedures was evaluated by analysis of Certified Reference Material BCR-701 and CRM 146R. A two-sided t-test was used to check for significant differences from the reference content. Table 5.4 shows the data of three replicate analyses obtained for *aqua regia* extraction.

Table 5.4: Results obtained (mean ± standard deviation, n=3) for sequential extraction analysis and *Aqua regia* extractable (pseudo-total) metal content of BCR 701 sediment.

	Step 1		Step 2		Step 3	
	Found value $mg.kg^{-1}$	Certified value $mg.kg^{-1}$	Found value $mg.kg^{-1}$	Certified value $mg.kg^{-1}$	Found value $mg.kg^{-1}$	Certified value $mg.kg^{-1}$
u	69.5±0.2	49.3±1.7	120±3	124±3	53.4±1.3	55.2±4
i	15.5±2	15.4±0.9	24±0.3	26.6±1.3	15.9±0.2	15.3±0.9
n	193.6±2.6	205±6	104±2	114±5	47.9±1	45.7±4

	Residual		Pseudo-total	
	Found value $mg.kg^{-1}$	Indicative value $mg.kg^{-1}$	Found value $mg.kg^{-1}$	Indicative value $mg.kg^{-1}$
u	37.3±2	38.5±11.2	271.8±5.1	275±13
i	42.1±3	41.4±4	100±1	103±4
n	105.1±2.7	95±13	449±2	454±19

Table 5.5 shows the revised BCR sequential extraction procedure, expressed as $mg.kg^{-1}$ of dry mass.

Table 5.5: Results obtained (mean ± standard deviation, n=3) for *Aqua regia* extractable (pseudo-total) metal content of CRM 146R sewage sludge from industrial origin.

Metal	Found Value $mg.kg^{-1}$	Certified value $mg.kg^{-1}$
Co	6.35±0.09	6.5±0.31
Cu	744±7	831±16
Mn	278±4	298±9
Ni	53.3±0.9	65±3
Zn	2887±29	3043±58

Uncertainty is expressed as standard deviations; the values obtained are not significantly ($P > 0.05$) different from the certified values. The data for pseudo-totals and fractionation of Cu and other elements were obtained from triplicates (n = 3) with mean ± standard deviation. The TSS and VSS concentrations were determined according to the APHA standard methods (APHA, 1995).

2.4.4. Visual Minteq

The geochemical equilibrium model Visual MINTEQ (Gustaffsson, 2004) was used to simulate the chemical speciation of Cu in solution in two different experiments (without and with EDTA addition) in the absence of anaerobic granular sludges. For calculation, the solid forms of Cu were allowed to precipitate. Visual MINTEQ is capable of calculating equilibrium aqueous speciation, precipitation and dissolution of minerals, complexation, adsorption, solid phase saturation states, etc. (Gustaffsson, 2004).

3. Results

3.1. Effect of electric current on Cu fractionation

Figure 5.2 shows the development of the electric potential gradient across the sludge matrix with time. The highest electrical potential gradient applied at a 5ml.min^{-1} flow rate of electrolytes was 3.5 V.cm^{-1}. During the experiments, the gradient increased from 0.04 to 3.5 V.cm^{-1} and then decreased to 1 V.cm^{-1} (Fig.5.2). Figure 5.2 represents all the experiments as there were similar electric potential gradients observed.

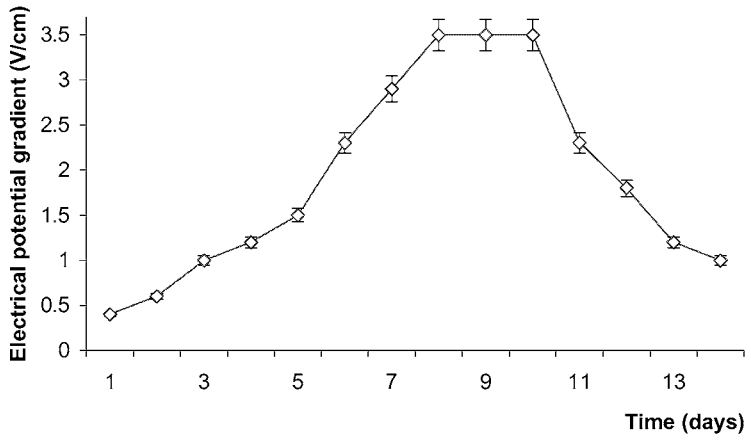

Figure 5.2. Evolution of the electrical potential gradient (V.cm^{-1}) with time (experiment C).

3.2. pH distribution in the sludge cake

Figure 5.3 presents pH distribution in the sludge cake with $Cu(NO_3)_2$ and CuEDTA as contaminants.

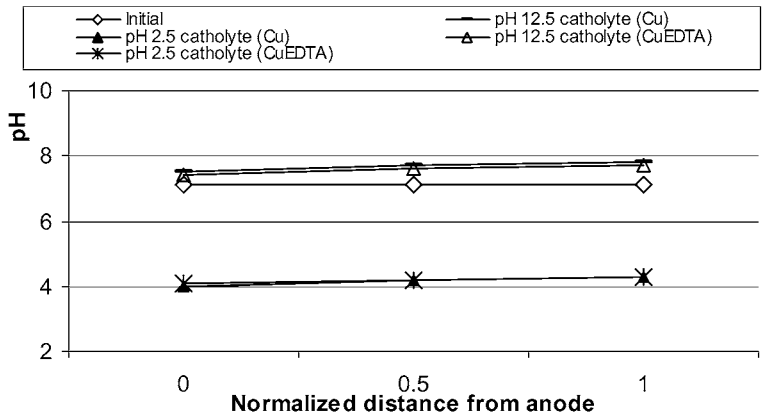

Figure 5.3. pH distribution in the sludge cake.

When the electrical potential was applied between two electrodes, hydrogen and hydroxyl ions were formed due to the electrolysis of water. According to Figure 5.3, when pH reached 12.5 in the catholyte, it was 7.5 in the sludge cake closer to the anode and increased till 7.8 when normalized distance from the anode was 1. During experiments with pH 2.5 in the catholyte, pH in the sludge cake was 4.0 closer to the anode and slightly increased to 4.3 when the normalized distance from the anode was 1 (Fig. 5.3).

3.3. Initial fractionation of Cu in anaerobic granular sludge

Table 5.6 presents the total concentrations and sequential extraction results from the experiments.

Table 5.6. Total concentrations and fractionation of heavy metals in the sludge cake after the electrokinetic treatment (mg.kg^{-1}).

Exp	Contam.	Sludge	Total concentration (after treatment)	Residual fraction	Organic/ sulfide	Oxide	Exchangeable/ Carbonate
A	Cu	Fresh	860±80	820±70	610±65	1030±102	510±44
B	Cu	Pre-inc.	890±85	1130±102	690±64	780±80	350±27
C	Cu	Fresh	860±80	930±86	590±55	590±42	1150±102
D	Cu	Pre-inc.	920±88	1080±103	560±50	760±57	1010±100
A'	CuEDTA	Fresh	720±75	1140±105	1460±182	270±23	340±27
B'	CuEDTA	Pre-inc.	770±77	1630±120	240±26	1130±109	330±25
C'	CuEDTA	Fresh	730±74	1360±127	1100±112	400±33	230±22
D'	CuEDTA	Pre-inc.	770±77	1420±180	640±57	580±44	490±45
A"	Zn	Fresh	123±14	155±22	85±8	54±6	40±6
B"	ZnEDTA	Fresh	125±14	135±12	65±7	55±6	40±6
C"	Co	Fresh	35±3	43±8	35±5	20±2	25±3
D"	CoEDTA	Fresh	35±3	40±8	35±5	20±2	25±3
E"	Ni	Fresh	39±5	52±6	20±2	18±2	36±4
F"	NiEDTA	Fresh	39±5	55±6	20±2	16±2	20±2
A*	Ca	Fresh	2080	840±70	510±45	2190±160	2330±123

B*	CaEDTA	Fresh	2000	750±65	1570±120	1400±140	1860±101
C*	Fe	Fresh	24000	26000±1500	18300±1200	12700±900	8700±210
D*	FeEDTA	Fresh	24400	21500±1200	20200±1200	16500±1100	13500±1120
E*	Mg	Fresh	620	260±44	240±43	390±49	510±45
F*	MgEDTA	Fresh	590	270±45	300±44	440±52	380±39

Prior to electrokinetic treatment (at pH 7.1), Cu was mainly associated with the exchangeable/carbonate (310 $mg.kg^{-1}$) fraction of fresh Cu supplemented granular sludge (Fig. 5.4a).

The remaining Cu was spread equally over the other fractions: 190 $mg.kg^{-1}$ of Cu in the residual and organic/sulfides and 200 $mg.kg^{-1}$ in the oxides fractions (Fig. 5.4a).

Pre-incubation of sludge with Cu prior to the electrokinetic treatment modified the Cu fractionation. The most abundant fractions in the pre-incubated sludge were, respectively, the oxides (330 $mg.kg^{-1}$) and the residual (260 $mg.kg^{-1}$) fractions (Fig. 5.4b). Addition of Cu and EDTA simultaneously resulted in a decrease in all fractions (Fig. 5.5), except in the exchangeable/carbonate fraction (310 $mg.kg^{-1}$), compared to the non-EDTA amended sludge (Fig. 5.4).

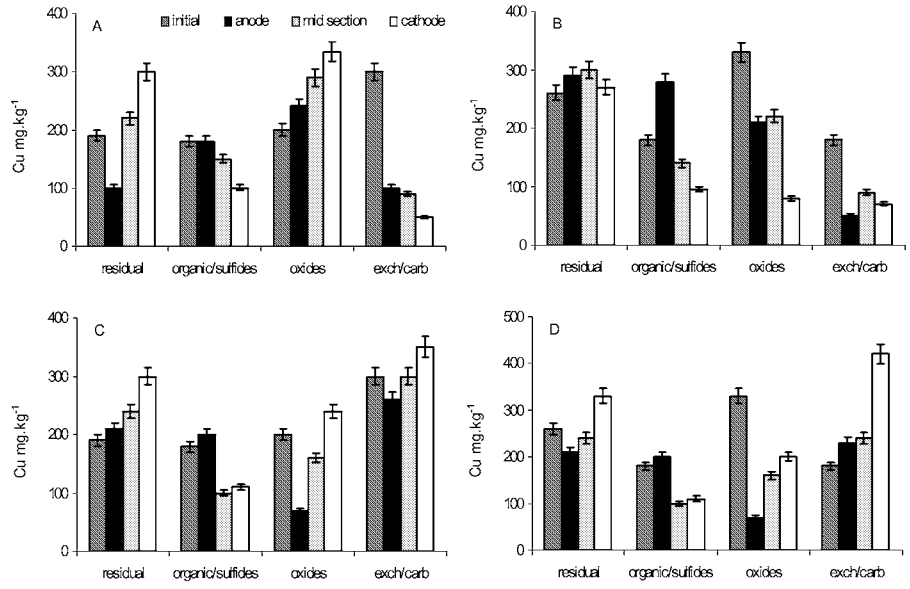

Figure 5.4. Effect of electrokinetic treatment on the Cu distribution in anaerobic granular sludge artificially contaminated with $Cu(NO_3)_2$: **A)** Fresh and **B)** pre-incubated sludge with pH 12.5 in the catholyte (final pH 7.7 in the sludge cake); **C)** Fresh and **D)** pre-incubated sludge with pH 2.5 in the catholyte (final pH 4.2 in the sludge cake).

After the electrokinetic treatment (0.15 $mA.cm^{-2}$ DC current for 14 days), the fractionation of Cu in the granular sludge matrix had changed significantly (Fig. 5.3 and 5.4). A significant increase of Cu in the residual (from 190 to 300 $mg.kg^{-1}$) and the oxides (from 200 to 320 $mg.kg^{-1}$) fractions was observed for the freshly amended sludge, which was directed towards the cathode (Fig. 5.3a). Cu associated with the exchangeable/carbonate fraction decreased from 310 to 80 $mg.kg^{-1}$, which moved towards the anode (Fig. 5.3a). One of the major trends was that the Cu concentration increased in the residual fraction of most of the experimental conditions at both the cathode and anode side (Fig. 5.3 and 5.4).

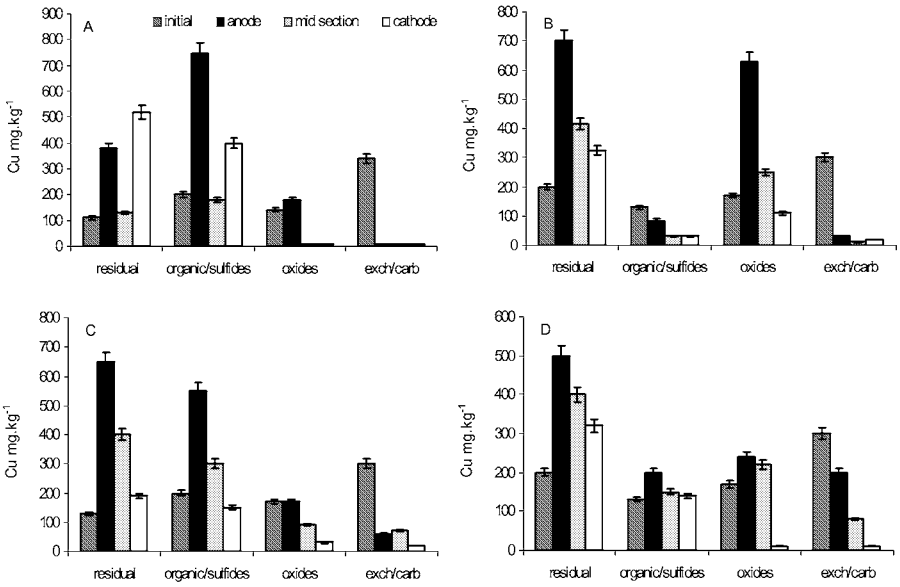

Figure 5.5. Effect of electrokinetic treatment on the Cu distribution in the anaerobic granular sludge artificially contaminated with CuEDTA. **A')** Fresh and **B')** pre-incubated sludge with pH 12.5 in the catholyte (final pH 7.7 in the sludge cake); **C')** Fresh and **D')** pre-incubated sludge with pH 2.5 in the catholyte (final pH 4.2 in the sludge cake).

3.4. Effect of pH during the electrokinetic treatment on the Cu fractionation

The major fractions with which Cu was associated after electrokinetic treatment with pH 12.5 in the catholyte solution (final pH 7.7 in the sludge bed) were the residual (up to 310 $mg.kg^{-1}$) and the oxides (320 $mg.kg^{-1}$) fractions, which were redistributed towards the cathode (Fig. 5.4a). However, after electrokinetic treatment, cumulative amount of oxide fraction from all the parts of the sludge in electrokinetic cell, was the highest (1030±102 $mg.kg^{-1}$), followed by the residual (820±70 $mg.kg^{-1}$) fraction (Table 5.6).

When the pH was maintained acidic (pH 2.5) in the electrolytes (final pH 4.2 in the sludge bed), the most abundant Cu fractions were the exchangeable/carbonates (330 mg.kg^{-1}) and the residual (300 mg.kg^{-1}) fractions, which moved towards the cathode (Fig. 5.4c). The Cu associated with the organic/sulfides (up to 210 mg.kg^{-1}) and oxides (up to 236 mg.kg^{-1}) fractions remained unchanged, respectively, at the anode and cathode side (Fig. 5.4c). The cumulative amount of the exchangeable/carbonate (1150±102 mg.kg^{-1}) and residual fraction (930±86 mg.kg^{-1}) was also found the highest in the sludge cake after the electrokinetic treatment (Table 5.6).

3.5. Effect of sludge pre-incubation on the Cu fractionation

When the sludge was pre-incubated with Cu for 30 days, the dominant fractions were the oxides (up to 320 mg.kg^{-1}), residual (290 mg.kg^{-1}) and organic/sulfides (up to 280 mg.kg^{-1}) upon the termination of the electrokinetic treatment at pH 12.5 in the catholyte (Fig. 5.4b). The Cu associated with the organic/sulfides fraction had migrated towards the anode (Fig. 5.4b). After the electrokinetic treatment, cumulative amount of the residual (1130±102 mg.kg^{-1}) and oxides (780±80 mg.kg^{-1}) fractions was prevailing in the sludge cake (Table 5.6).

The major fractions of Cu were the exchangeable/carbonates (390 mg.kg^{-1}) and residual (up to 320 mg.kg^{-1}) when the pH in the catholyte solution was set to pH 2.5 (final pH 4.2 in the sludge cake). Interestingly, Cu in the exchangeable/carbonates and the residual fractions moved towards the cathode, in contrast to Cu bound to the organic/sulfides fraction, which migrated towards the positively charged anode (Fig. 5.4d). Cumulative amounts of residual and oxide (1080±103 mg.kg^{-1} and 1010±100 mg.kg^{-1}, respectively) fractions were also predominant after the electrokinetic treatment (Table 5.6).

3.6. Effect of EDTA on the Cu fractionation after electrokinetic treatment

Table 5.7 shows that in the presence of EDTA, Cu accumulated at both sides compared to the initial concentration. This is an opposite trend compared to the non EDTA treated sludge. When the pH in the catholyte solution was 12.5 (final pH 7.7 in the sludge water), there was a significant decrease in all fractions (Fig. 5.5a') except the exchangeable/carbonates fraction, which remained the same as in the Cu nitrate amended sludge experiments (310 mg.kg^{-1}) (Fig. 5.4a).

After electrokinetic treatment, the most predominant fraction was the organic/sulfides fraction (from 170 to 750 mg.kg^{-1}), which had moved towards the positively charged anode (Fig. 5.5a'). An increase in the residual fraction (from 110 to 390 and 550 mg.kg^{-1}) was also observed simultaneously at the anode and cathode sides and it was the highest at the cathode (Fig. 5.5a'). There was also a significant increase in the cumulative amount of the organic/sulfides and the residual (1460±182 mg.kg^{-1} and 1140±105 mg.kg^{-1}, respectively) after the electrokinetic treatment (Table 5.6).

When the pH in the anolyte solution was 2.5 (final pH 4.2 in the sludge), the major fractions of Cu in the electrokinetically treated EDTA amended fresh sludge were the residual (650 mg.kg^{-1}) and the organic/sulfides (550 mg.kg^{-1}) fractions, which were directed towards the anode (Fig. 5.5c'). The cumulative amounts show similar distribution trends (Table 5.6).

After electrokinetic treatment of the pre-incubated sludges at a pH 12.5 in the catholyte (final pH 7.7 in the sludge bed) in the presence of EDTA, Cu was mainly present in the residual (up to 680 mg.kg^{-1}) fraction, followed by the oxides (640 mg.kg^{-1}) fraction (Fig. 5.5b') at the anode side. At pH 2.5 in the catholyte (final pH 4.2 in the sludge bed), the most significant Cu fraction (490 mg.kg^{-1}) was the residual fraction at the anode side (Fig. 5.5d'). The same trend can be observed in cumulative amounts of different fractions, presented in Table 5.6.

3.7. Effect of electrokinetic treatment on trace and macroelements

3.7.1. Trace elements

Initially, the main trace metal fraction was the residual (Fig. 5.6a", c" and e"): Zn-78 $mg.kg^{-1}$, Co-15 $mg.kg^{-1}$, Ni- 30 $mg.kg^{-1}$ (Table 5.4). After electrokinetic treatment at pH 12.5 in the catholyte, the residual fraction decreased significantly for Zn and Ni but not for Co (Fig. 5.6a", c" and e").

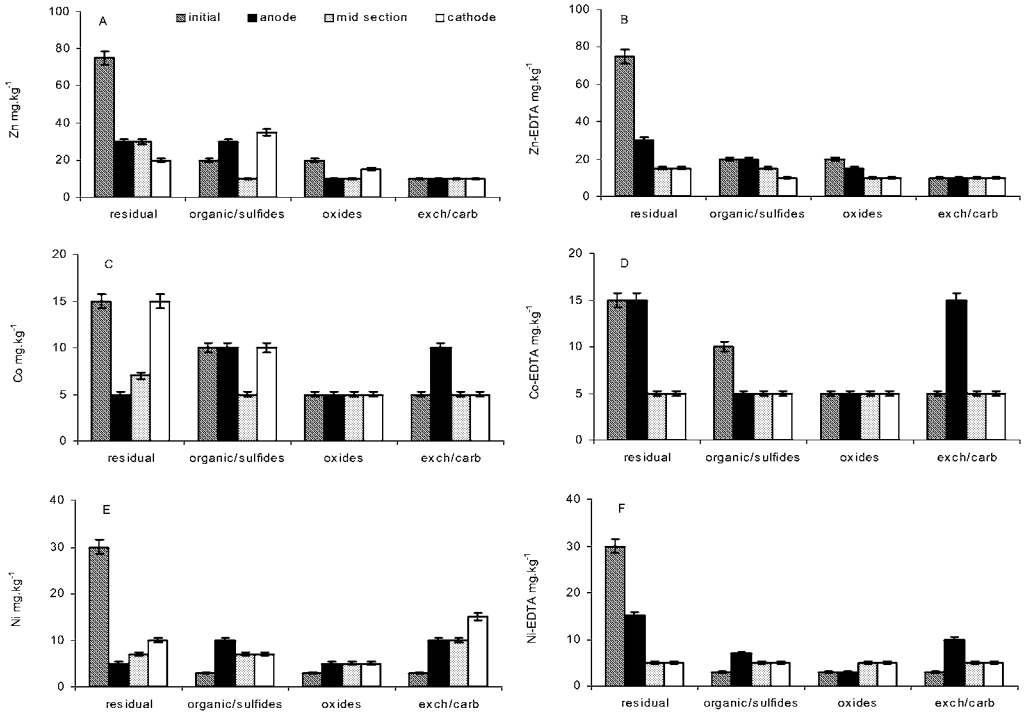

Figure 5.6. Fractionation of trace metals in electrokinetically treated anaerobic granular sludge with pH 12.5 in the catholyte (final pH 7.7 in the sludge bed): **A"), C"), E")** $Cu(NO_3)_2$ contaminated sludge and **B"), D"), F")** CuEDTA contaminated sludge.

There was only an increase in the organic/sulfides fraction from 20 to 38 $mg.kg^{-1}$ at the cathode for Zn (Fig. 5.6a") and from 3 to 10 $mg.kg^{-1}$ for Ni, which was directed towards the anode (Fig. 5.4e). Also, a significant increase in Ni associated with the exchangeable/carbonates fraction (from 3 to 15 $mg.kg^{-1}$) occurred at the cathode (Fig. 5.6e"). Co associated with the exchangeable/carbonates fraction increased from 5 to 10 $mg.kg^{-1}$ after the electrokinetic treatment at the anode side (Fig. 5.6c"). However, the other fractions (i.e. oxides and organic/sulfides fractions) of Co remained without any significant changes at the cathode or anode sides (Fig. 5.6c"). However, cumulative amounts of Zn, Ni and Co in fractions show different results (Table 5.6). There was a significant increase in the residual fraction of Zn,

Ni and Co (155±22 mg.kg^{-1}, 52±6 mg.kg^{-1} and 43±8 mg.kg^{-1}, respectively) after the electrokinetic treatment (Table 5.6).

The presence of EDTA during electrokinetic treatment influenced the fractionation of trace metals (Fig. 5.6b", d", f"). There was a significant decrease (from 78 to 15 mg.kg^{-1}) in Zn and Ni (from 30 to 5 mg.kg^{-1}) associated with the residual fraction (Fig. 5.6b" and 5.6f"). In contrast, a significant accumulation of Co (from 5 to 14 mg.kg^{-1}) in the exchangeable/carbonate fraction was observed (Fig. 5.6d"). In addition, there was an increase in the organic/sulfides (from 3 to 7 mg.kg^{-1}) and in the exchangeable/carbonate Ni (from 3 to 11 mg.kg^{-1}) fractions (Fig. 5.6f"). EDTA amendment induced a redistribution of Co and Ni towards the anode in the exchangeable/carbonates fraction upon electrokinetic treatment. After the EDTA addition and electrokinetic treatment, the cumulative amount of the residual fraction of Zn, Ni and Co remained the most prevailing (Table 5.6).

3.7.2. Macro elements

For the macro-elements the major initial fractions were the oxides (Fig. 5.7a*, c*, e*): Ca – 1200 mg.kg^{-1}, Mg – 300 mg.kg^{-1} and the residual for Fe (10000 mg.kg^{-1}) (Table 5.7). After electrokinetic treatment, the residual fraction had increased for Ca from 180 to 400 mg.kg^{-1} (Fig. 5.7a*) but decreased for Fe from 10000 to 6000 mg.kg^{-1} (Fig. 5.7c*). The most abundant Ca fraction was the exchangeable/carbonates (Fig. 5.7a*) attributing to 900 mg.kg^{-1}, which moved towards the cathode. The Mg fractionation showed a significant increase in the exchangeable/carbonates (300 mg.kg^{-1}) and organic/sulfides (130 mg.kg^{-1}) fractions (Fig. 5.7e*), which had also moved towards the cathode. The most abundant cumulative amount of Ca was found in exchangeable/carbonate (2330±123 mg.kg^{-1}), Fe in the residual (26000±1500 mg.kg^{-1}) and Mg in the exchangeable/carbonate (510±45 mg.kg^{-1}) fractions (Table 5.6).

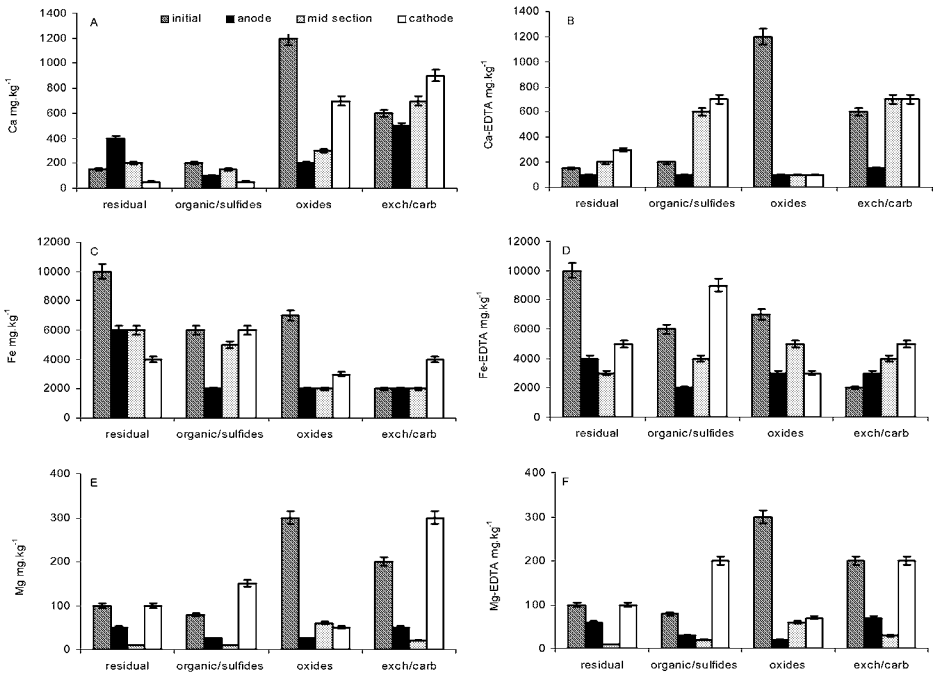

Figure 5.7. Fractionation of macroelements in electrokinetically treated anaerobic granular sludge with pH 12.5 in the catholyte (final pH 7.7 in the sludge bed): **A*), C*), E*)** $Cu(NO_3)_2$ contaminated sludge and **B*), D*), F*)** CuEDTA contaminated sludge.

There was a significant decrease observed for all Fe associated fractions, which moved towards the cathode, with exception of the residual fraction (Fig. 5.7c*). Electrokinetic treatment of CuEDTA exposed sludge influenced the fractionation of Ca, Mg and Fe (Fig. 5.7b*, d* and f*). The most significant increase for Ca, Mg and Fe was in the organic/sulfides fraction: 600 $mg.kg^{-1}$, 200 $mg.kg^{-1}$ and 8500 $mg.kg^{-1}$, respectively (Fig. 5.7b*, d* and f*). Ca associated with the exchangeable/carbonates fraction increased from 600 to 700 $mg.kg^{-1}$ (Fig. 5.7b*), which was directed towards the cathode. The addition of CuEDTA did not influence the cumulative amounts of Ca and Fe in the sludge cake, having the residual fraction the most abundant (Table 5.6). Nevertheless, cumulative amount of Mg was found most associated with oxides (440±52 $mg.kg^{-1}$) fraction (Table 5.6).

4. Discussion

This study showed that electrokinetic treatment at 0.15 $mA.cm^{-2}$ for 14 days not only induces Cu and trace metals mobility but also alters their fractionation in anaerobic granular sludge. The latter is strongly influenced by the pH, contamination aging and the presence of EDTA. The discussion section describes successively the Cu fractionation prior to electrokinetic treatment and the effect of different working conditions during electro-remediation on the partitioning of Cu and some macro and microelements in the sludge.

4.1. Cu fractionation before and after electrokinetic treatment

Addition of Cu as easily soluble salt resulted in a much higher total Cu concentration in the sludge compared to all other heavy metals. In all cases, Cu was more or less evenly distributed between the four operationally defined fractions of the BCR protocol. The distribution of Cu was very similar to that observed for Cu in the non-Cu-spiked sludges used to prepare the amended anaerobic granular sludge (Osuna et al. 2004), which was also used in the current study. However, the proportion of Cu present in the two most easily extracted fractions (exchangeable/carbonates and oxides fractions) was much larger due to increasing Cu concentrations in the sludge (Fig. 5.4 and 5.5 and Table 5.6). Both low and high Cu concentrations show a very strong affinity for the organic matter / sulfides and residual fractions of the BCR scheme (van Hullebusch et al., 2005). It is, indeed, well known that Cu strongly interacts with organic matter and sulfides (Pattrick et al., 1997; Lu and Allen, 2002; Vulkan et al., 2002).

In natural sediment, soil or sludge, the metals bound to the sulfides are mainly leached in the organic/sulfides fraction (Lacal et al., 2003). In anaerobic matrixes, several different Cu sulfide minerals can coexist in the sludge matrix (Pattrick et al., 1997). Insoluble complexes as chalcocite (Cu_2S) can be formed in the presence of sulfide (Morse and Luther, 1999). Cu may be also adsorbed in large quantity at the surface of pyrite minerals (Müller et al., 2002), however little evidence has been found in the literature for Cu accumulation in the crystalline lattice of the Fe sulfides. In the same time, Cu may also undergo biosorption by cell membrane surfaces with proteins and acid groups that serve as binding site (Hayes and Theis, 1978).

When the fresh Cu amended sludge was supplemented with EDTA prior to electrokinetic treatment, the initial fractionation of Cu changed (Fig. 5.5a' and 5.5c') and a lower initial total Cu quantity accumulated in the sludge was noticed (Table 5.7). This is in agreement with the work of Osuna et al. (2004) who study the effect of EDTA on the accumulation of Co in the same anaerobic granular sludge.

As depicted in Table 5.6, after the electrokinetic treatment, the total amount of Cu decreased in the experiments with Cu and CuEDTA as contaminant. It is hypothesized that the reason for such a decrease in concentration may be that Cu, present in prevailing exchangeable/carbonate and in lesser extend oxides fractions (Fig. 5.5a' and c') was solubilized by the electric current and migrated to the sludge solution.

Also, the possible exchange of Cu between different fractions could have occurred and altered the fractionation after the electrokinetic treatment was applied. Indeed, Ribeiro and Mexia (1997) observed that when sequential extraction was applied to Cu-contaminated soil, the most important mobilization of Cu occurred from exchangeable/carbonate fraction. Also, they argued that electricity induces the mobility of strongly bound fractions such as organic/sulfide and amorphous Fe-oxides towards the loosely bound fractions and finally to the 'solution' where they are ready to migrate towards the cathode. However, there were no attempts to verify the exchange between different fractions during this particular study.

Table 5.7: Initial trace and major elements concentrations with $Cu(NO_3)_2$ or Cu EDTA in the fresh anaerobic granular sludge before the electrokinetic treatment and removal efficiencies at a final pH of 4.2 in the sludge cake. The number in brackets means that there was depletion in comparison to the initial heavy metal concentration. Accumulation means that there was n % more heavy metals accumulated than present initially.

$Cu(NO_3)_2$	Initial concentrations (in sludge granules)	Concentrations at the anode ($mg.kg^{-1}$ dry sludge and removal efficiencies (%)	Concentrations at the cathode ($mg.kg^{-1}$ dry and removal efficiencies (%)
Cu	1070±60	620 (40)	785 (27)
Zn	125±12	60 (52)	78 (37)
Co	38±0.5	34 (11)	40 (accumulation) 10
Ni	38±0.5	36 (5)	41 (accumulation) 11
Ca	2100±120	1100 (48)	2000 (5)
Fe	25000±300	12000 (52)	16000 (36)
Mg	680±42	150 (78)	580 (15)
Cu EDTA	Initial concentrations (in sludge granules)	Concentrations at the anode (mg/kg) and removal efficiencies (%)	Concentrations at the cathode (mg/kg) and removal efficiencies (%)
Cu	790±40	1320 (accumulation) 67	980 (accumulation)
Zn	125±12	70 (44)	50 (60)
Co	38±0.5	42 (accumulation) 11	33 (16)
Ni	38±0.5	40 (accumulation) 10	36 (5)
Ca	2100±120	350 (83)	1900 (10)
Fe	25000±300	11000 (56)	19000 (24)
Mg	680±42	40 (94)	590 (16)

It was predicted that the addition of EDTA should increased the amount of dissolved Cu according to the Cu speciation simulations (Fig. 5.8).

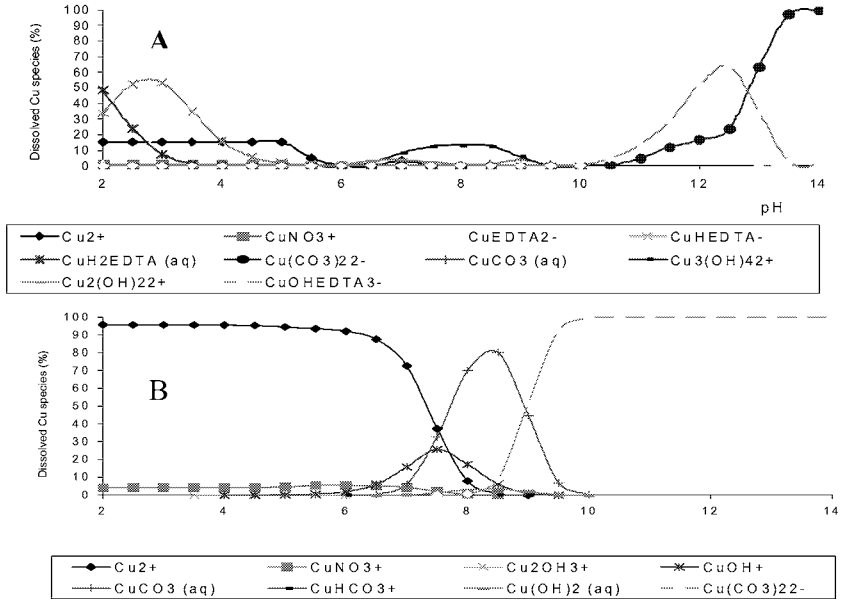

Figure 5.8. Dissolved Cu species distribution as a function of pH with **A)** and without EDTA **B)** in absence of anaerobic granular sludges.

At pH 7.7, the addition of EDTA increased the percentage of dissolved Cu from 1% to 83.5% of the total Cu initially present in the systems prior to electrokinetic treatment (Fig. 7.8).

Nevertheless, electrokinetic experiments showed that the addition of EDTA failed to increase the Cu amount in easily soluble fractions (Table 5.6).

4.2. Effect of pH on Cu fractionation

The pH influences the absorption and desorption, precipitation, dissolution and speciation reactions of Cu. At low pH, Cu tends to desorb from the sludges and dissolves as positively charged ions (Hsiau and Lo., 1998). All heavy metals have a specific pH underneath which their solubility may increase. For Cu, this pH is 5.5 in calcareous and non-calcareous soils, however the exact pH depends on the type of the matrix (Martinez and Motto, 2000). The acidification of the sludge cake during the electrokinetic treatment consequently promoted the formation of soluble mobile Cu compounds such as free Cu (Cu^{2+}, Fig 5.8b) which caused Cu accumulation at the cathode side of either the freshly amended (Fig. 5.4c) and pre-incubated sludge (Fig. 5.4d). According to the species distribution model, the main dissolved species are Cu^{2+} when the pH is acidic (Fig. 5.8b).

These positively charged metal ions migrate towards the cathode in the exchangeable / carbonates and residual fractions of the freshly amended (Fig. 5.4c) and pre-incubated sludge (Fig. 5.4d). Also at neutral and slightly alkaline pH (6.5 – 7.5), the predominant dissolved species are positive charged compounds, e.g. Cu^{2+}, Cu_2OH^{3+} and $CuOH^{+}$ (Fig. 5.8b). These Cu species can migrate towards the negatively charged cathode, as observed for the oxides and residual fractions of the freshly amended sludges (Fig. 5.4a).

4.3. Effect of EDTA on Cu fractionation

The addition of the chelating agent EDTA to the sludge cake resulted in a change of the migration direction of Cu in the applied electric field (Fig. 5.5). Complexing agents like EDTA are widely used for the enhanced removal of heavy metals from different contaminated media without (Nirel et al., 1998; Sillanpää et al., 2001; Nowack, 2002) and with (Wong et al., 1997; Velizarova et al., 2002) electrokinetic treatment. EDTA has proved to be an efficient chelating agent since it forms stable complexes with most metals, especially with transition metals over a broad pH range (Lo and Yang, 1999). It can also be utilized for both desorption of sorbed ions and dissolution of precipitated metal compounds (Papassiopi et al. 1999).

For a final pH of 7.7, the addition of EDTA increased the accumulation of Cu at both the cathode (from 790 to 980 $mg.kg^{-1}$) and at the anode side (from 790 to 1320 $mg.kg^{-1}$) (Table 5.7). Cu extracted was shown to increase in the organic / sulfides and residual fractions at the anode and cathode sides of the freshly Cu amended sludge for a final pH of 7.7 (Fig. 5.5a') and surprisingly only at the anode side at final pH 4.2 (Fig 5.5c'). At acidic pH, the concentration of Cu in cationic form is expected to increase (Fig. 5.8) but, in contrast to this theoretical calculation, when the final pH in the sludge bed is about 4.2, Cu extracted in the organic / sulfides and residual fractions only increased at the anode side (Fig. 5.5c').

This outlines the presence of negatively charged Cu species. When the sludge was pre-incubated with Cu for 30 days and then supplemented with EDTA before electrokinetic treatment, Cu extracted in the residual and oxides fractions exclusively increased at the anode side at both pH conditions (Fig. 5.5b' and 5.5d'). This also outlines the presence of negatively charged Cu species. According to the species distribution model (Fig. 5.8a), the main dissolved species are $CuEDTA^{2-}$ and $Cu_3(OH)_4^{2+}$ at neutral and slightly alkaline pH (pH 6 – 8). At acidic pH (pH 2 – 4), the most abundant dissolved species are $CuEDTA^{2-}$, $CuHEDTA^{-}$ and Cu^{2+} (Fig. 5.8b). The prevailing Cu complexes are negatively charged, thus they migrate towards the

positively charged anode (Fig. 5.5), which is also reported for Cu mobility in clayey soils (Hamed et al., 1991).

Fig. 5.5 shows that EDTA is efficient to decrease the Cu content in the exchangeable /carbonates and oxides fractions of the fresh sludge, however no decrease was noticed in the organic sulfide and residual fractions. This is probably due to the presence of sulfide precipitates which are efficient sorbants. Consequently, they can prevent Cu removal from the anaerobic sludge as reported by Reddy and Chinthamreddy (1999) when they introduced sulfide in kaolin.

4.4. Effect of pre-incubation on Cu fractionation

After a 30 days incubation period, an increase of Cu in the residual fraction has been noticed very likely due to the contamination aging effect (McLaren and Clucas, 2001) instead of electricity. The mobility of Cu decreases with the duration (a few hours) of its contact with anaerobic sludge due to the formation of Cu sulfide crystals (Pattrick et al., 1997). The electrokinetic treatment of the pre-incubated Cu amended sludges mainly influenced the metal accumulated in the organic / sulfides fraction (Fig. 5.4b-d). Kim et al. (2002) found that the organic / sulfides fraction is relatively mobile in an electric field, which is in agreement with Fig. 5.4b and in a lesser extend with Fig. 5.4d.

It is well documented that Cu has also an extremely strong affinity to form complexes with the organic matter present (Bolan et al., 2003; Lu and Allen; 2002, Vulkan et al., 2002). When Cu is associated with the organic fraction it usually forms negative compounds, e.g. Cu-Org^{2-} or Cu-Org^{-} (Lu and Allen, 2002; Vulkan et al., 2002). Watson et al. (2004) showed that organic compounds such as EPS of sewage sludge were hydrolyzed in a sulfidic environment in about 24 hours. Hydrolysis of the organic sludge matrix thus very likely occurred during the pre-incubation step of the Cu amended anaerobic sludges resulting in a release of organic compounds bound with Cu. Vulkan et al. (2002) showed that Cu in water extracts of activated sludge was found almost exclusively in negatively charged low molecular weight (below 1000 Da) complexes. This would explain the accumulation of Cu at the anode side in the organic / sulfides fraction (Fig. 5.4b).

4.5. Effect of electrokinetic treatment on trace metals and major elements fractionation

An increase of the Co and Ni content, present in much lower concentrations than Cu in the exchangeable/carbonates fraction in comparison the initial concentration (Fig 5.6 c" and e") was noticed when the final pH in the sludge bed was 7.7. This might be explained by the desorption of trace metals from the sludge crystalline matrix (i.e., residual fraction) or from organic/sulfide fraction due to the application of electric current, which also induces a pH change (Kim et al., 2002; Jakobsen et al., 2004). Nonetheless, the most prevailing fraction remained to be the residual, therefore it is hypothesized that neither pH (4.2 in the sludge cake) nor the addition of EDTA were sufficient in solubilizing Zn, Co and Ni from the sludge granules.

The removal of trace metals from the residual and organic/sulfides fractions are, however, not complete. Reddy and Chinthamreddy (1999) showed that the introduction of sulfides into kaolin caused a significant decrease in migration of Ni(II) due to NiS precipitation. The presence of sulfides in anaerobic granular sludge can thus explain why trace elements are only partially removed from the organic/ sulfides and residual fractions (Fig. 5.6). It is important to note that sulfides may not only be present in the organic/sulfides fraction but also as crystalline sulfide minerals (Patrick et al., 1997) in the residual fraction.

The electrokinetic treatment at a final pH of the sludge of 7.7 increased the Ca, Fe and Mg content in the exchangeable/carbonates fraction at the cathode side from 500 to 800 $mg.kg^{-1}$ for

Ca, from 2000 to 2700 mg.kg^{-1} for Fe and from 170 to 280 mg.kg^{-1} for Mg (Fig. 5.7a*, c*, e*) when $Cu(NO_3)_2$ was used as contaminant suggesting that Fe, Mg and Ca were solubilized from the sludge matrix or were exchanged from other fractions and therefore moved through the sludge cake in cationic forms. This is consistent with the findings of Suèr et al., (2003) where electromigration of heavy metals was discussed in the soils.

As observed for Cu, the trace metal content was higher at the cathode side for the non-EDTA-treated sludge, in contrast to the trace metal content at the anode side for EDTA treated sludge (Table 6.7). This difference is likely linked to the formation of trace metal species with different charge in the presence of EDTA, as shown in the species distribution model for Cu (Fig. 5.8). Further research using speciation techniques at molecular level, e.g. X-ray diffraction and energy dispersive X-ray spectroscopy spectra with scanning/transmission electron photographs or X-ray absorption spectroscopy (Huang et al., 2003) can help to develop a further understanding of changes in anaerobic granular sludges chemical composition and mineralogy before and after electrokinetic treatment. A compilation of these results will provide a fundamental approach for geochemical modelling and assist in the development of effective electrokinetic remediation systems.

5. Conclusions

The present study on electrokinetic treatment of methanogenic granules showed that:

- The migration in the applied electric field strongly depends on the fractionation in the sludge.
- Application of low-level direct current (0.15 mA.cm^{-2} for 14 days) induces mobility of Cu species in a methanogenic granular sludge cake.
- Under the applied electric field and in the absence of EDTA, Cu and trace metals (Zn, Co and Ni) migrate towards the cathode, except when anaerobic granular sludge is pre-incubated with Cu.
- In presence of EDTA, Cu, Zn, Co and Ni migrate towards the anode during electrokinetic treatment. EDTA addition does not affect the direction of migration of Ca, Fe and Mg.
- The addition of EDTA did not result in the increase of Cu in most soluble and hence most easily mobilized exchangeable/carbonate and oxide fractions. Thus, lower pH conditions and EDTA lead to an increase of the Cu content in the less mobile fractions (i.e. residual and organic / sulfides fractions).

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CHAPTER 6: ELECTROKINETIC COPPER AND IRON MIGRATION IN ANAEROBIC GRANULAR SLUDGE

Virkutyte, J.[1,2], Sillanpää, M.[2] and Lens, P.[1]*

[1] Sub-department of the Environmental Technology, University of Wageningen, 'Biotechnion' - Bomenweg 2, PO Box 8129, 6700 EV Wageningen, The Netherlands.
[2] University of Kuopio, Department of Environmental Sciences, Laboratory of Applied Environmental Chemistry, PO Box 181, 50101 Mikkeli, Finland
*The corresponding author [email: piet.lens@wur.nl, tel. +31 317483339, fax: +31 317482108].

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Abstract

The application of low-level direct electric current (40 mA) as electrokinetic technique to treat copper contaminated ($Cu(NO_3)_2$ or $CuEDTA^{2-}$ with initial copper concentration of 1000 mg kg^{-1} wet sludge) mesophilic anaerobic granular sludge was investigated. The experimental sludge was obtained from a full scale UASB reactor treating paper-mill wastewater. The effects of different pH and EDTA concentrations on the migration of copper and iron during electrokinetic treatment were evaluated as well. The distribution efficiencies were evaluated by calculating difference between initial contaminant concentration and the accumulated concentration by the electrodes. The distribution and migration direction of copper contaminant significantly depended on the pH of the sludge cake or the copper complexation with EDTA. In an 'open' cell, (sludge cake in contact with air), the highest copper mobilities were observed at pH 2.5 in both $Cu(NO_3)_2$ or CuEDTA amended sludge, corresponding to the highest contaminant accumulation at the cathode (22(±2)% and 8(±2)% at the anode, respectively. The highest accumulation of iron was achieved with $Cu(NO_3)_2$ as contaminant and accounted to 24(±2)% of accumulation at the cathode. When EDTA was amended to the sludge, the highest iron accumulation (8(±2)%) was found also at the cathode. In a 'closed' cell (no sludge cake contact with air), the highest accumulation was obtained for CuEDTA in fresh (4(±0.5)% and 2(±0.05)%) sludge at the anode at a final pH of 4.2 and 7.7 in the sludge cake, respectively.

Keywords: electromigration, copper, iron, granular sludge, pH

1. Introduction

It is well documented that contamination of the environment with heavy metals, radionuclides and hazardous organic compounds is growing every year mainly due to inefficient waste handling techniques, hazardous waste leakage from landfills (Hernandez et al., 2003; Sheppard et al., 2000; Dijkstra, 1998), surface runoffs as well as domestic and industrial effluents (Mulligan et al., 2004). Due to increased environmental pollution, there is a continuous search for the most efficient, sustainable and environmentally friendly technique to remediate contaminated media. During the past decades, several new and innovative solutions for the clean-up of soils and sediments, solid waste, wastewater and sludge have been developed (Hashimoto et al., 2004, Abramovitch et al., 2003).

One of these emerging technologies are electrokinetic remediation techniques, which offer a great potential for the removal of charged contaminants from sludge (Kim et al., 2002), soil (Virkutyte et al., 2004, Ottosen et al., 2002, Acar and Alshawabkeh, 1993) and copper chromated arsenate (CCA)-treated timber waste (Velizarova et al., 2002). The electrokinetic phenomenon employs a low-level direct current across the contaminated medium, which induces the mobility of charged contaminants due to electromigration and electro-osmotic flow (Virkutyte et al., 2004, Haran et al., 1996, Mattson and Lindgren, 1995). The electrokinetic technique is a beneficial technology because it is includes low power consumption, control over the water flow direction and dissolved contaminants and the confinement of contaminants in the electrode chambers that makes easier the subsequent treatment (Acar and Alshawabkeh, 1993).

As an essential element, copper is required by organisms for a wide range of metabolic processes (Fjällborg and Dave, 2003). Iron is an important nutrient too (Ito et al., 2000). High levels of both metals are, however, hazardous for biota (Mulligan et al., 2004). Hence, it is important to control their amount in the environment (Mercer et al., 2001) and thus to develop cost-effective techniques for their removal from contaminated media.

The aim of this study was to examine the electrokinetic mobility of copper and iron in anaerobic granular sludge, a porous medium consisting of anaerobic microbial consortia used in upflow anaerobic sludge bed (UASB) reactors for wastewater treatment (Hulshoff Pol et al., 2004), under different experimental conditions. Laboratory scale experiments were conducted in two different electrokinetic cell layouts containing anaerobic granular sludge, artificially contaminated with copper. The effect of different pH, cell layout, draining, $EDTA^{4-}$ addition on the electromigration efficiency were examined.

2. Materials and Methods

2.1. Source of biomass

Anaerobic granular sludge was obtained from a full-scale UASB reactor (Industriewater Eerbeek B.V., Eerbeek, The Netherlands) treating paper-mill wastewater (Lens et al., 1999). Table 6.1 presents the main characteristics of the experimental sludge used for the experiments.

Table 6.1. Main characteristics of the experimental sludge (van Hullebusch et al., 2005; Osuna et al., 2004) (TSS - Total Suspended Solids, VSS - Volatile Suspended Solids).

Parameter	Amount
Mean density	1040 $kg.m^{-3}$
Water content	40%
Background copper concentration ($mg.kg^{-1}$ TSS)	150 (±5.6)
Background iron concentration ($mg.kg^{-1}$ TSS)	3880 (±800)
(TSS	22.6% (±0.2%)
VSS	73.9% (±0.2%)
pH	7.1
Carbonates (% of TSS)	0.4 (±0.2)
Total sulfur ($mg.g^{-1}$ TSS)	41.8 (±1.0)
Total phosphorus ($mg.g^{-1}$ TSS)	6.6 (±0.1)

For electrokinetic experiments, anaerobic granular sludge was amended with 3.78 g of $Cu(NO_3)_2$, dissolved in 50 ml anaerobic demi-water (T = 22(±1)°C, pH = 7.1), which resulted in a copper contamination of 1000 mg Cu kg^{-1} (wet sludge). In $CuEDTA^{2-}$ amended experiments, 3.78 g of Na_2H_2EDTA (molar ratio of Cu^{2+}:$EDTA^{4-}$ was 1.2:1 mol L^{-1}) was dissolved in 50 ml demi-water and added simultaneously with $Cu(NO_3)_2$.

The $Cu(NO_3)_2$ (and Na_2H_2EDTA) containing solution was in contact with the biomass for 48 hours (Reddy et al., 1997), during which it was thoroughly mixed. After the contamination procedure was over, this sludge, still suspended in the copper (EDTA) containing supernatant, was mounted in the electrokinetic set-up. Approx. 200 ml of demi-water was added to fully saturate the sludge cake. For experiments with drained sludge, the supernatant of the sludge was decanted, after which the copper loaded sludge was fully saturated in demi-water and mounted in the electrokineti cell.

2.2. Electrokinetic set-up

Experiments were conducted in an 'open' and 'closed' (Ottosen and Hansen, 1992) electrokinetic set-up (Fig. 6.1). In the 'open' cell, the granular sludge cake was continuously in

contact with the air, whereas no air was in contact with the granular sludge cake mounted in the 'closed' set up.

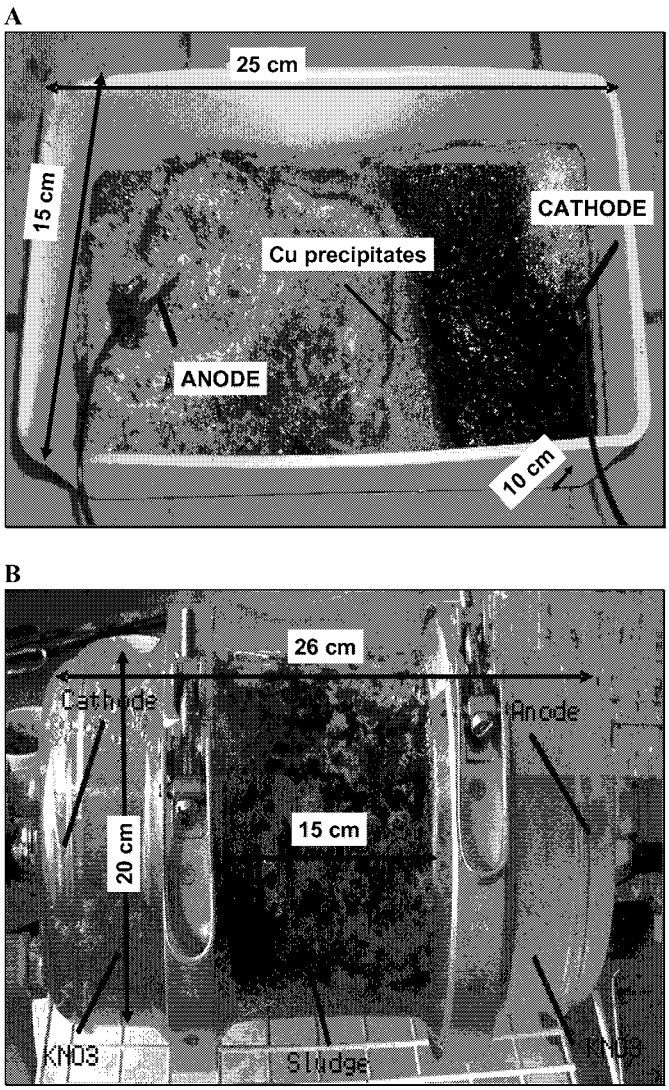

Figure 6.1. A) The 'open' electrokinetic set up and **B)** The 'closed' electrokinetic set up.

In the 'open' electrokinetic cell, the stainless steel (diameter 3 mm; length 5 cm) electrodes (supplied by Elektronika-WUR, the Netherlands) were immersed directly into the sludge cake (Fig. 6.1a). In the 'closed' electrokinetic cell (Fig. 6.1b), the central compartment was separated from the anode and cathode compartments by, respectively, anion-exchange (IA1-204SXZL386) and cation-exchange (IC1-61CZL386) membranes (Ionics Inc, Watertown, Massachusetts, USA). The anode and cathode were immersed into a 0.05 M KNO_3 conductive

solution (Fig. 6.1b). The electrodes (diameter 3 mm, length 5 cm) were titanium bars (supplied by Elektronika-WUR, the Netherlands).

2.3. Experimental design

The amount of sludge placed in both the 'open' and 'closed' electrokinetic cells was 1000 g (wet sludge). The outer dimensions of the 'open' electrokinetic cell was length 25 cm, width 15 cm and height 15 cm. The layer of the sludge was 10 cm thick. The internal diameter of the 'closed' cell was 20 cm (Fig. 6). Variations in experimental conditions are presented in Table 6.2.

Table 6.2. Experimental conditions of laboratory scale experiments.

Parameters / Experiments	A	B	C	D	E	F	A'	B'	C'
Electrokinetic cell setup	'open'	'open'	'open'	'open'	'open'	'open'	'open'	'open'	'open'
Sludge	drained, fresh	non drained, fresh	drained, fresh	non drained, fresh	drained, fresh	non drained, fresh	non drained, fresh	non drained, fresh	non drained, fresh
Distance between electrodes (cm)	22	22	22	22	22	22	22	22	22
Length of sludge cake (cm)	25	25	25	25	25	25	25	25	25
Initial concentration ($mg.kg^{-1}$) in the sludge*	850(±50)	1150(±150)	850(±50)	1150(±150)	850(±50)	1150(±150)	1150(±150)	1150(±150)	1150(±150)
Contaminant	$Cu(NO_3)_2$	$Cu(NO_3)_2$	$Cu(NO_3)_2$	$Cu(NO_3)_2$	$Cu(NO_3)_2$	$Cu(NO_3)_2$	CuEDTA	CuEDTA	CuEDTA
Membranes	No	No	No	No	No	No	No	No	No
pH at the cathode	12.5	12.5	7.7	7.7	2.5	2.5	12.5	7.7	2.5
Current strength (mA)	40	40	40	40	40	40	40	40	40
Voltage (V)	10-30	12-28	10-28	12-30	10-30	10-30	12-28	12-30	10-30
Duration (days)	14	14	14	14	14	14	14	14	14

Parameters / Experiments	I	II	III	IV
Electrokinetic cell setup	'closed'	'closed'	'closed'	'closed'
Sludge	non drained, fresh	non drained, fresh	non drained, fresh	non drained, fresh
Distance between electrodes (cm)	17	17	17	17
Length of sludge cake (cm)	15	15	15	15
Initial concentration ($mg.kg^{-1}$)	1150(±150)	1150(±150)	1150(±150)	1150(±150)
Contaminant	$Cu(NO_3)_2$	$Cu(NO_3)_2$	CuEDTA	CuEDTA
Membrane	Ion exchange	Ion exchange	Ion exchange	Ion exchange

pH in the catholyte	12.5	2.5	12.5	2.5
Current strength (mA)	40	40	40	40
Voltage (V)	10-28	10-30	10-30	12-30
Duration (days)	14	14	14	14

* Initial concentration of Cu is presented with the natural Cu content and without the Cu amount in the sludge liquid in experiments with sludge drainage.

Electrokinetic remediation of the artificially contaminated sludge occurred at room temperature (T = 22±1°C) for 14 days. In all experiments, the current strength in the sludge was 40 mA. Throughout the treatment process, the voltage and the pH were monitored.

The initial pH of the sludge cake was 6.9. After spiking it reached 7.1. When the pH fluctuations were uncontrolled in the 'open' cell, the pH reached 12.5 at the cathode and 2.5 at the anode after electrokinetic treatment. To examine the effect of pH on the migration of copper and iron, pH was set manually to 2.5 or 7.7 in the sludge cake by 1 M HNO_3 addition at the cathode of the 'open' cell. When the pH fluctuations were uncontrolled in the electrolytes of the 'closed' cell, it reached 12.5 and 2.5 in the catholyte and anolyte, respectively. This gave a final average pH of 7.5 – 7.7 in the sludge cake upon termination of the electrokinetic treatment. When the pH in the catholyte was set to 2.5 by 1 M HNO_3 addition, the average pH in the sludge cake after the homogenization of samples, was 4.0 – 4.2 upon termination of the electrokinetic treatment.

At the end of the electrokinetic treatment, the power supplies were turned off, the electrode wires were disconnected and the electrokinetic cell was disassembled. Sludge samples were taken from the electrokinetic apparatus and sliced into five slices with a stainless steel serrated knife. The pH values, copper and iron concentrations were determined in each slice. There were 1.5 cm of the sludge behind each electrode and 22 cm in front of each electrode in the 'open' electrokinetic cell.

2.4. Analyses

Each sludge slice was thoroughly homogenized prior to analysis. The pH of the sludge cake slices were measured as reported by Acar and Alshawabkeh (1996) by directly inserting a pH electrode into the sludge.

The total metal concentration in the homogenized anaerobic granular sludge samples (expressed as mg metal kg^{-1} dry weight) after electrokinetic treatment was determined after microwave destruction and aqua regia (HCl/HNO_3, 3:1) digestion (Matthews CEM 2100, North Caroline, USA) as described by Virkutyte et al. (2005). The digestion procedure was carried out in three steps (15 min at 100°C, 15 min at 150°C and 30 min at 200°C). After digestion, the concentrations of total metals were analyzed by The Atomic Absorption Spectroscopy (AAS) flame (Perkin-Elmer 300).

For the determination of Cu and Fe in the sludge solution, the portion of the sludge by the electrodes was filtered through 0.45 μm filter and Cu and Fe content was measured using Perkin-Elmer 300 atomic absorption spectrophotometry (FAAAS).

2.5. Quality assurance

The analysis of samples followed the standard quality assurance and control (QA/QC) procedures (Segura et al., 2004). To ensure the accuracy of the experimental results, new

electrodes, ion exchange membranes and tubing were used for the each experiment. After each experiment, electrokinetic cells were immersed into the 0.05 M HCl solution for 24 h, soaked in a tap water container for 24 h and rinsed with deionized water to avoid cross contamination between experiments (Reddy and Chinthamreddy, 2003). The reliability of the chemical analysis was done by three replicate determinations of copper and iron and the range of recoveries was 95 – 106%. The AAS-flame calibration was checked after testing every five samples and mass balance analysis was performed for each test.

2.6. Copper and iron distribution among experimental fractions calculations

Copper and iron distributions among experimental fractions were calculated for each final pH. Distribution was calculated from their concentrations in the liquid phase, in the sludge granules and the metal deposited onto the electrodes. The data of total copper and iron concentrations were obtained from triplicates (n = 3).

3. Results

3.1. Evolution of overall voltage

Upon introducing the low level current to a granular sludge cake in the 'open' cell, there was an increase in the voltage during the first days (from 17 V to 20 V). After approx. 6 days, the voltage drop to 18 V was followed by a constant increase in voltage to 30 V until it was stabilized at that value after 12-14 days of electrokinetic treatment. Then it decreased to 10 V (Fig. 6.2). The evolution of voltage gradient is demonstrated for selected experiment. The changes in voltage gradient were similar in all the experiments in both 'open' and 'closed' cells with constant current (Table 6.2).

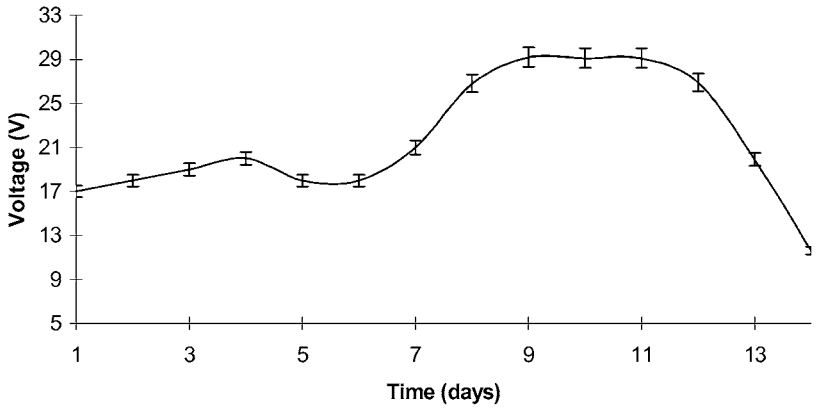

Figure 6.2. Example of typical evolution of voltage gradient during electrokinetic treatment of anaerobic granular sludge (experiment F).

3.2. Effect of sludge liquid drainage on the copper and iron migration in the 'open' cell

When the copper contaminated solution was removed (drained sludge), the direction of the copper migration was unclear and copper remained distributed throughout the sludge cake without a defined movement (Fig. 6.4a – b). Also the iron distribution was undefined, i.e. it was either spread in the electrokinetic cell (Fig. 6.4a and b) or slightly shifted towards the cathode (Fig. 6.4c).

The copper and iron concentration in the decanted sludge solution was 190 mg L^{-1} and 780 mg L^{-1}, respectively, prior to the electrokinetic treatment. Upon the termination of the electrokinetic treatment (final pH of 4.2 in the sludge cake), the copper concentration was 110 mg L^{-1} and 200 mg L^{-1}, respectively, at the anode and cathode in the sludge solution (Fig. 6.3). In addition, the soluble iron concentrations amounted to 600 mg L^{-1} and 760 mg L^{-1}, respectively, at the anode and cathode (Fig. 6.3).

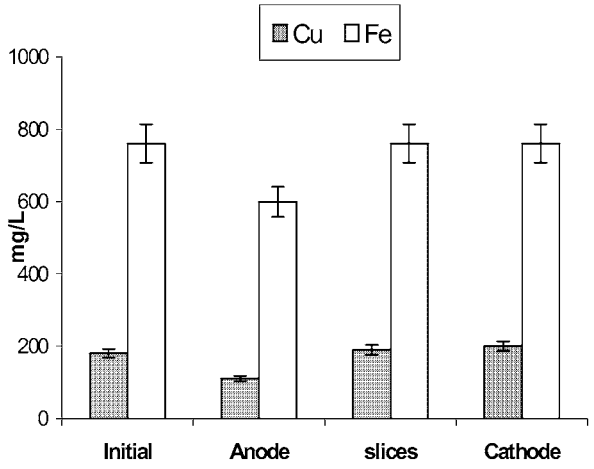

Figure 6.3. Initial amount of copper and iron in the sludge solution ('open' electrokinetic cell) prior to the electrokinetic treatment and the amount after the electrokinetic treatment (final pH 2.5 in the sludge cake).

3.3. The pH jump in the 'open' electrokinetic cell

During the experiments in the 'open' cell, when the pH was extremely alkaline (10.5 – 12.5) or neutral (6.6 – 7.7) at the cathode side of an 'open' electrokinetic cell (with $Cu(NO_3)_2$ as contaminant), blue copper precipitates were observed upon the termination of the experiments (Fig. 6.1a). When the pH was adjusted to 2.5 at the cathode, no precipitates were observed. However, there were no visible precipitates when CuEDTA was used as contaminant. Also, no visible blue precipitates were observed in the sludge cake of the 'closed' electrokinetic cell at the different pH conditions tested. Figure 6.4 presents variations in the pH in the sludge cake.

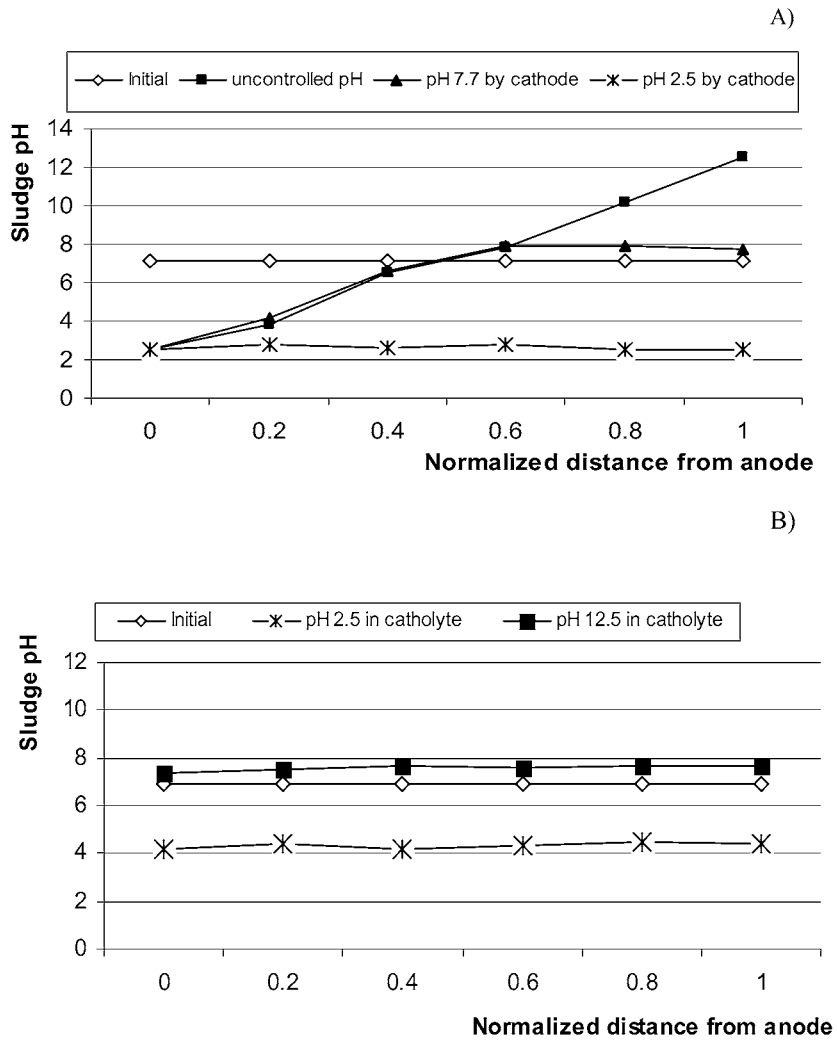

Figure 6.4. pH distribution in the sludge cake: A) 'open' and B) 'closed' electrokinetic cell.

The pH jump in the 'open' electrokinetic cell appeared at a normalized distance from the anode of 0.6 - 0.8 (Fig. 6.4). However, there were no pH jump observed in the experiments, conducted in the 'closed' electrokinetic cell, regardless the pH conditions (Fig. 6.4).

3.4. Effect of the pH on the copper and iron migration in the 'open' cell

When the pH was extremely alkaline (9.2 – 12.5), no mobility of copper or iron were observed (Fig. 6.5a) in drained sludge. However, when the sludge solution was not drained, there was pronounced movement of Fe towards the cathode (Fig. 6.5.b).

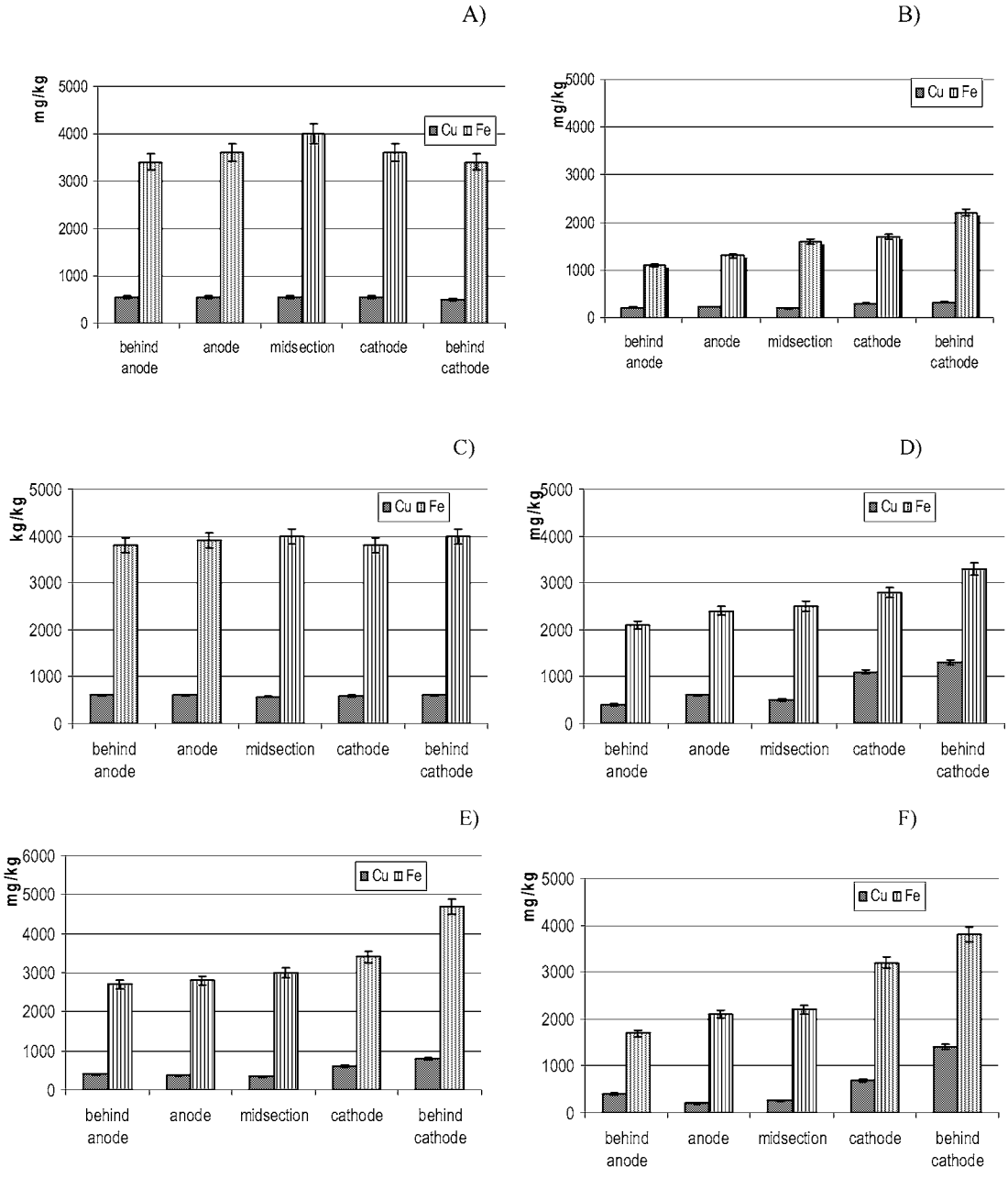

Figure 6.5. Effect of electrokinetic treatment in an 'open' cell on the copper and iron distribution in anaerobic granular sludge artificially contaminated with $Cu(NO_3)_2$: **A)** Drained and **B)** Non-drained fresh sludge with pH 12.5 at the cathode; **C)** Drained and **D)** non-drained fresh sludge with pH 7.7 at the cathode; **E)** Drained and **F)** Non-drained fresh sludge with pH 2.5 at the cathode.

When the pH was maintained slightly alkaline (7.7) or acidic (2.5), the migration of copper and iron (Fig. 6.5c and 6.5d) was directed towards the negatively charged cathode. Copper and iron moved towards the cathode during electrokinetic treatment of non-drained sludge at pH 7.7 and 2.5 (Fig. 6.5e–f).

The movement of copper was significant in experiments with a final pH of 7.7 and 2.5 (4(±1)% and 22(±2)% accumulation of contaminant, respectively) of the sludge cake (Table 6.3a). The same pattern was observed for iron, where at the final pH of 2.5 in the sludge cake, the highest accumulation of iron at the cathode was 4(±1)% more than the initial concentration (Table 6.3b).

Table 6.3a. Copper iron concentrations (mg kg^{-1}) and distribution efficiencies in an 'open' electrokinetic cell. Values between the brackets are the distribution efficiencies (%), i.e. the value is either x % less (depletion) or x % more (accumulated) than initially present in the sludge.

Metal	Name of the experiment	Initial concentration (in the sludge cake)	pH	Concentration at the anode	Concentration at the cathode
			Fresh drained sludge		
Cu	A	850	12.5	600 (30)	500 (41)
Cu	C	850	7.7	600 (30)	650 (24)
Cu	E	850	2.5	300 (65)	800 (6)
			Fresh non-drained sludge		
Cu	B	1150	12.5	300 (74)	400 (65)
CuEDTA	A'	1150	12.5	800 (30)	700 (39)
Cu	D	1150	7.7	450 (61)	1200 (accum) 4
CuEDTA	B'	1150	7.7	800 (30)	600 (48)
Cu	F	1150	2.5	300 (74)	1400 (accum) 22
CuEDTA	C'	1150	2.5	1250 (accum) 8	300 (74)

Table 6.3b. Iron concentrations (mg kg^{-1}) and distribution efficiencies in an 'open' electrokinetic cell. Values between the brackets are the distribution efficiencies (%), i.e. the value is either x % less (depletion) or x % more (accumulated) than initially present in the sludge.

Metal	Name of the experiment	Initial concentration	pH	Concentration at the anode	Concentration at the cathode
			Fresh drained sludge		
Fe	A	3880	12.5	3200 (18)	3000 (23)
Fe	C	3880	7.7	3800 (2)	4200 (acumm) 8
Fe	E	3880	2.5	2700 (30)	4800 (accum) 24
			Fresh non-drained sludge		
Fe	B	3880	12.5	1200 (69)	2300 (41)
FeEDTA	A'	3880	12.5	1200 (69)	2500 (36)
Fe	D	3880	7.7	2200 (43)	3300 (15)
FeEDTA	B'	3880	7.7	3000 (23)	2100 (46)
Fe	F	3880	2.5	1400 (64)	4000 (acumm) 4
FeEDTA	C'	3880	2.5	1900 (51)	4200 (acumm) 8

Table 6.3c. The copper and iron concentrations (mg kg^{-1}) and distribution efficiencies (%) using the 'closed' electrokinetic cell. Values between the brackets are the distribution efficiencies (%), i.e. the value is either x % less (depletion) or x % more (accumulated) than initially present in the sludge.

Initial concentration (Cu) (mg kg^{-1})	Name of the experiment	pH		Concentration at the anode and distribution efficiencies	Concentration at the cathode and distribution efficiencies
Distribution efficiencies		Catholyte cake	Sludge		
			Fresh sludge		
Cu 1150	I	12.5	7.7	600 (48)	800 (30)
CuEDTA 1150	II	12.5	7.7	1100 (accum) 2	900 (22)
Cu 1150	III	2.5	4.2	700 (39)	900 (22)
CuEDTA 1150	IV	2.5	4.2	1200 (accum) 4	400 (65)

3.5. Effect of EDTA on copper and iron migration in the 'open' cell

The migration of the EDTA complexed copper ions was opposite to the migration when copper was added to the sludge as $Cu(NO_3)_2$. At pH 12.5, copper showed some migration, however this may be attributed to the random fluctuations as copper forms insoluble compounds at alkaline pH. At pH 7.7 and 2.5, copper migrated towards the anode (Fig. 6.6c'. and 6.7). Iron (Fig. 6.6b') also migrated towards the anode in the presence of EDTA at pH 7.7.

When copper was complexed with EDTA, the copper distribution efficiency towards the cathode was considerably lower than towards the anode (Table 6.3a). The highest accumulation was found at the anode at a final pH 2.5 of the sludge cake (8(±1)% more than initially present). The migration of iron was also more directed towards the anode than to the cathode (Table 6.3b). The highest distribution efficiency was when the final pH of the sludge cake was 2.5 and the accumulation of iron at the cathode reached 8(±1)% more than initially was present in the sludge. Therefore the EDTA addition did not enhance the Cu removal from anaerobic granular sludge as the highest accumulation without the presence of EDTA was 22%((±2)% (Table 6.3a) and in a presence of EDTA, the accumulation reached only (8(±1)%.

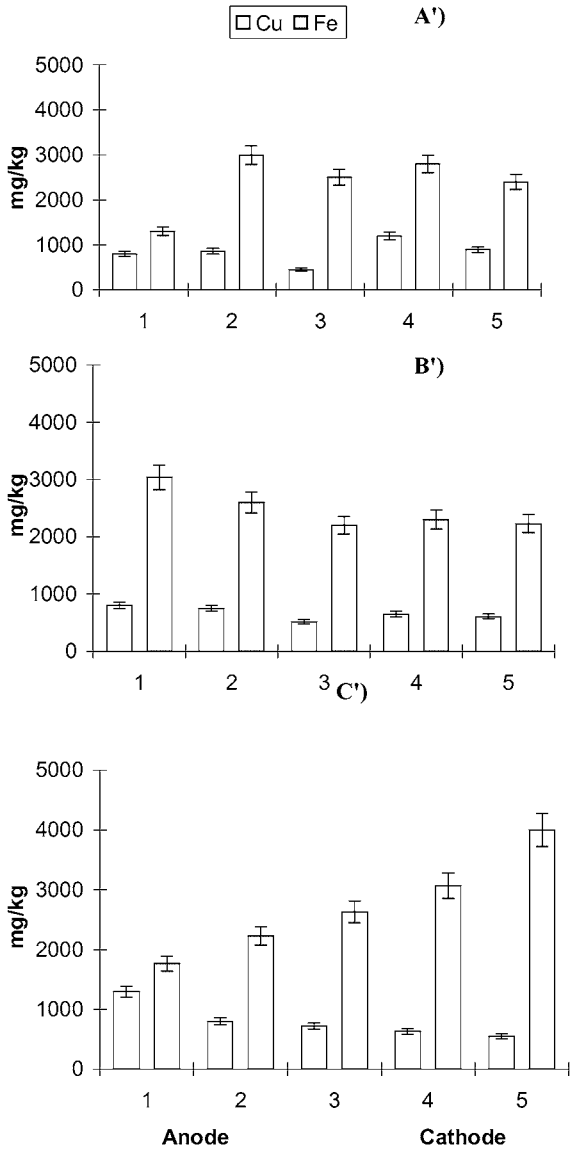

Figure 6.6. Effect of electrokinetic treatment in an 'open' cell on the copper and iron distribution in the anaerobic granular sludge artificially contaminated with CuEDTA. **A')** Fresh sludge with pH 12.5 at the cathode; **B')** Fresh sludge with pH 7.7 at the cathode and **C')** Fresh sludge with pH 2.5 at the cathode. (Numerals represent the slices of the sludge cake).

3.6. Copper transport in the 'closed' electrokinetic cell layout

Copper depletion amounted to 48±2% at the anode and 30±2% at the cathode, in the 'closed' cell, at a final pH of 7.7 in the sludge cake (experiment I, pH 12.5 in the catholyte). When the pH was lowered to 2.5 in the catholyte (experiment II, final pH of 4.2 in the sludge cake), copper migrated from the anode (39(±2)% depleted) to the cathode (22(±2)%) (Table 6.3c).

When the sludge was amended with $CuEDTA^{2-}$ (experiment III, final pH of 7.7 in the sludge cake), copper accumulated (2(±0.5)% at the anode and depleted (22(±2)%) at the cathode, respectively (Table 6.3c). Moreover, in the 'closed' cell (experiment IV, final pH 4.2 in the sludge cake), copper accumulated (4(±2)% more than initially present) at the anode and depleted (65(±2)% less than initially present) at the cathode (Table 6.3c).

3.7. Copper and iron distribution among selected experimental fractions in the 'open' electrokinetic cell

Figure 6.8 presents the average amounts of copper and iron in the sludge solution, granules and deposited onto the electrodes. According to Figure 6.8, the pH has a significant influence on the copper and iron distribution among the metal concentration in the sludge liquid and granules. Copper and iron were also found to be significantly deposited onto the electrodes when the pH of the system was kept acidic and slightly alkaline.

When the pH is acidic, there is a significant amount of copper and iron associated with the sludge granules. However, when the pH increased to a final pH of 12.5 in the sludge cake after the electrokinetic treatment, a considerable portion of copper and iron was found in the sludge solution (Fig. 6.8).

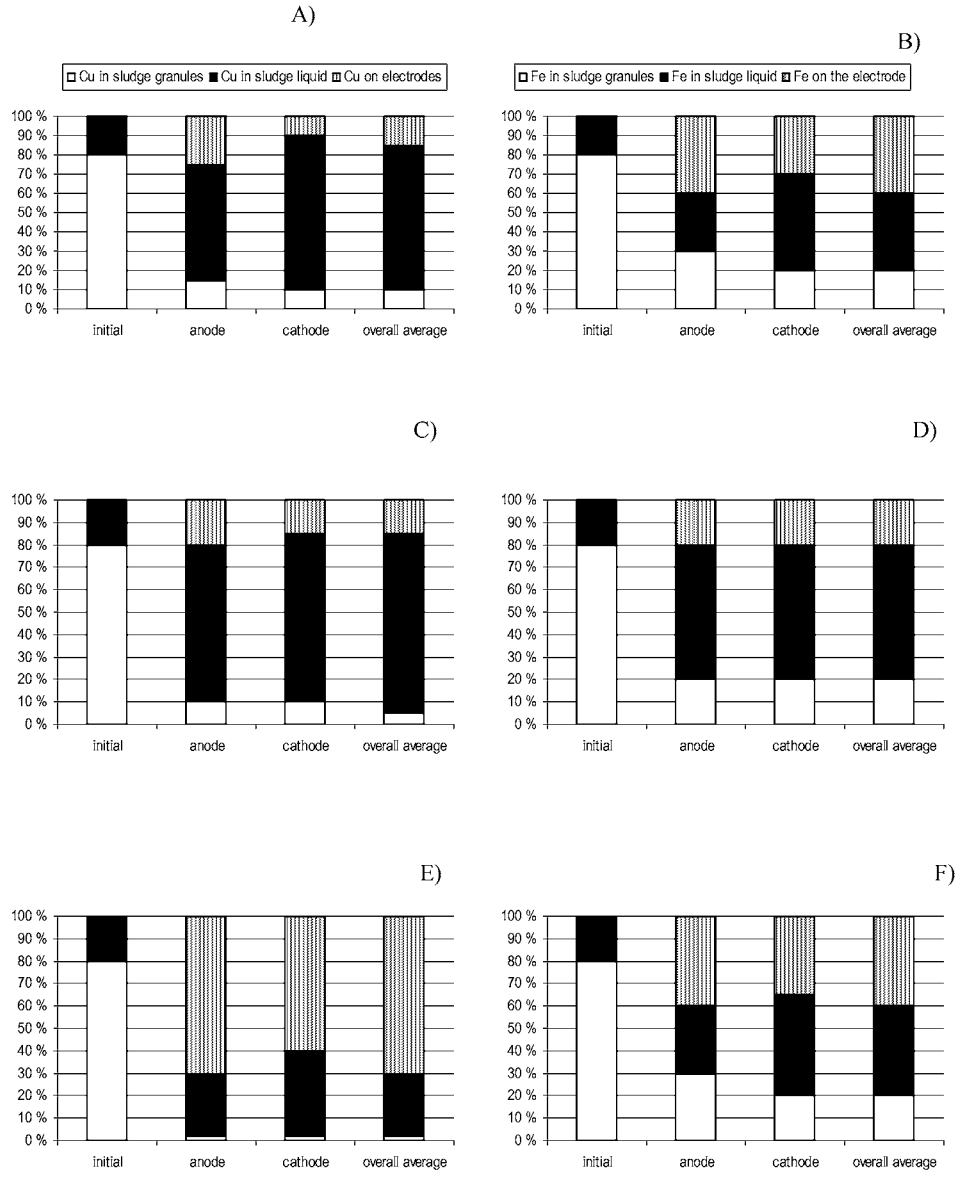

Figure 6.8. Distribution of Cu among selected experimental fractions in the 'open' cell A) final sludge pH 2.5; C) final sludge pH 7.7; E) final sludge pH 12.5 and Fe B) final sludge pH 2.5; D) final sludge pH 7.7 and F) final sludge pH 12.5.

4. Discussion

4.1. Variation of the overall voltage

As the electric current, which passes through the sludge cake is proportional to the voltage drop between the electrodes, the current of 40 mA was set constant and maintained during all experiments. When the voltage was applied to the electrodes, hydrogen and hydroxyl ions were formed. Generation of hydrogen at the anode leads to the acidification of the medium and affects the release of contaminants from the matrix. Kim et al. (2002) showed that Cu is released and is mobile in the electric field when the pH is acidic. This suggests that higher Cu removal efficiencies may be achieved in low pH environments.

There were no significant differences between the voltage fluctuations in the 'open' and 'closed' cells. This is consistent with the findings of Turer and Genc (2005), where rectangular and circular electrokinetic units were used to evaluate the effects of different parameters on the efficiency of Pb, Zn and Cu removal from soils.

Voltage fluctuations during electrokinetic treatment are related to the changing resistivity between the anode and cathode (Ottosen et al., 2002). According to Ohm's law ($V = I \times R$, where I is current and R is resistivity), the voltage increases when the resistivity or current increases. Due to the electrolysis of water, the sludge cake is gradually acidifies and the electrical resistance decreases due to electrochemical exchange reactions on the surface of the granules.

The increase in voltage (Fig. 6.2) means that the H^+ front formed at the anode migrates through the sludge (Ottosen et al., 2002, Velizarova et al., 2002). Therefore the increase in the resistance may be attributed to the copper and iron precipitates in the high pH areas. Also, the increase in the resistance may be due to the formation of non-conducting gaseous bubbles on the surface of electrodes due to the electrolysis of water reactions (Sah and Chen, 1998).

The small decrease of the voltage after 4 days of operation was observed due to lack of charged particles at the beginning of electrokinetic experiments. This is consistent to the observation of Velizarova et al. (2004) where she discussed possible reasons for the drop in voltage in the electrodialytic cell.

Voltage fluctuations were similar in experiments with and without drainage of the sludge solution. It was expected that there will be no initial voltage drop in the experiments without the drainage of the sludge solution because of the significant amount of ions in the sludge solution, which kept the conductivity high. However, the voltage drop was still observed (data not shown). The author hypothesized that this decrease could be attributed to the rapid complexation of formed H^+ and OH^- by sludge matrix and copper as well as iron ions. This rapid initial complexation removed ions that transport charge therefore the decay in voltage was observed.

The increase in voltage after 7 days of operation was observed (Fig. 6.2) because of the formation of excess H^+ by the anode, which moved through the sludge cake and increase in the copper and iron hydroxide concentrations. Indeed, Lee and Yang (2000) showed similar voltage fluctuations in the electrokinetic Pb removal from contaminated soils. The voltage increased due to increase in $Pb(OH)_2$ concentration by build-up of excess OH^- in the pore fluid near the cathode.

Consequently, the decrease in the voltage in the sludge upon termination of the experiment (Fig. 6.2) was due to the H^+ front reaching the cathodic side, where is meets the OH^- (Velizarova et al., 2002).

4.2. The pH jump in 'open' and 'closed' electrokinetic cell setups

It has been widely reported in the literature that the transport rate of hydrogen ions is almost twice the mobility of hydroxyl ions (Acar and Alshawabkeh, 1993). Therefore, the position of a pH jump, an area where drastic change in pH occurs, is always takes place close to the cathode. During the electrokinetic treatment process, due to the electrolysis of water, the pH in the close vicinity of the cathode increases significantly (pH = 11 - 12.5) due to the transport of hydroxyl ions from the cathode. Formed hydroxyl ions migrate through the soil and this alkaline front may have detrimental effects on the electrokinetic treatment efficiency.

Kim et al. (2005) discovered that the decrease of the electrokinetic treatment effectiveness may be attributed to the possible formation of metal precipitates (Cu, Fe, Zn, Ni, Co, Cd in particular) and increase of adsorbed and immobile metal species. The location of the pH jump, among other parameters, may also be influenced by the concentration and mobilities of ions present in the matrix though affecting the distribution of electric fields and formation of hydroxide complexes (Li et al., 1997).

There was no pH jump observed in the 'closed' electrokinetic cell (Fig. 6.4b). This could be attributed to the conditioning of cathode with HNO_3 solution.

The visible blue precipitates were observed (Fig. 6.1) in the experiments without drainage of the sludge solution (the 'open' electrokinetic cell) at pH 12.5, due to that most of the copper present in the solution precipitates as hydroxides when the pH gets extremely alkaline. On the contrary, when the solution is drained out, copper will be mainly associated with the sludge matrix. Ito et al. (2000) argued that copper has an extremely strong affinity to organic matter and tends to bind or absorb to the carbonates present in the sludge and this may influence the formation of the blue precipitates.

4.3. Copper and iron migration at high cathode pH

The observed migration of copper in the electrokinetic cells is a net movement of copper species present in both the sludge solution and the sludge granules. The amount of copper found in the sludge solution after the spiking was 17(±2)% from initial copper concentration in the sludge (Fig. 6.7), which suggests that a considerable amount of copper remained in a free ionic state or were bound to the soluble fractions in the sludge. However it is in contrast to findings of Kim et al. (2002), who determined that Cu has an extremely strong affinity to organic matter present in sludge. Therefore it forms Cu-organic complexes which are relatively insoluble.

The mobility of copper and iron in the 'open' (pH 12.5 and 7.7) and 'closed' (pH 12.5 in the catholyte attributing to a final pH of 7.7 in the sludge cake) electrokinetic cells and the efficiency of the electrokinetic distribution of copper and iron in the sludge were low (Table 6.3a and b) compared to the migration of the contaminants at acidic pH (final pH 2.5 in the sludge cake, 'open' cell). This is most probably due to the formation of insoluble and hence immobile species. Indeed, due to the electrolysis of water, the OH^- ions formed at the cathode significantly raise the pH of the system (Fig. 6.5 and 6.6). If the pH in the sludge cake is kept at neutral and / or alkaline conditions, copper will precipitate in the form of hydroxides and oxy-hydroxides ($Cu(OH)_2^0$), sulfides and carbonates (Hernandez et al., 2003). Additionally, iron also tends to precipitate as hydroxides and oxy-hydroxides, which are barely soluble when the pH of the system is higher than 7 (Mercer, 2001; Straub et al., 2001; Alloway, 1995).

4.3. Copper and iron migration at low cathode pH

When the pH was adjusted to 2.5 in the 'open' electrokinetic cell (Fig. 6.5), copper as well as iron was clearly transported towards the cathode with final copper and iron concentrations of, respectively, 20(±2)% and 5(±2)% higher than the initial concentration (Table 6.3a and b). This movement was due to the electromigration of copper species, which moves the copper compounds towards the electrodes due to their charges (Table 6.4a). It is well documented that when pH is acidic, copper is solubilized from the soil (Yeung et al., 1997; van Cauwenberghe, 1997) and sludge (Kim et al., 2002) matrices, forming positively charged species, which migrates to the negatively charged cathode. The reason for high distribution efficiencies and pronounced transport behavior of Cu and Fe is the availability of positively charged species such as Cu^{2+} or $Cu(OH)^{+}$ and Fe^{2+}/Fe^{3+}, which, under the applied electric field, moved through the sludge cake (Table 6.4b) according to their charges.

Therefore in order to solubilize Cu and Fe species and initiate the migration in the sludge matrix, it is necessary to adjust pH at the cathode.

4.4. Effect of pH on the $CuEDTA^{2-}$ migration

Chelating agents such as $EDTA^{4-}$ have proved to be the most efficient extractants, which form negatively charged compounds with heavy metals (Yeung et al., 1997).

When the pH in the sludge was maintained at 12.5, EDTA addition did not induce the movement of either copper or iron species (Fig. 6.6a'). This is due to the formation of insoluble complexes, as reported by Popov et al. (1999). On the contrary, at the final pH of 7.7 in the sludge, copper migration towards the anode occurred, which can be attributed to the formation of $CuEDTA^{2-}$ complexes (Nowack, 2002; Sillanpää et al., 2001).

When the pH is neutral and slightly acidic, copper forms negative compounds with EDTA ($CuEDTA^{2-}$, $CuHEDTA^{-}$, $CuOHEDTA^{-}$) and carbonates ($Cu(CO_3)_2^{2-}$) (Osuna et al., 2004; Bolan et al., 2003). According to their charges, negative compounds move towards the anode under the influence of an electric field. In addition, at pH 2.5, the migration of iron and copper to the anode (Fig. 6.6c') suggests that transport of $CuEDTA^{2-}$ and $FeEDTA^{2-}$ prevails. This is in agreement with Xue et al. (1995), where the transport of metal complexes with EDTA was discussed. Yuan and Weng (2003) argued that complexes as $FeOOH\text{-}EDTA\text{-}Cu^{-}$ can contribute to the copper transport towards the anode. The current study also observed similar migration pathway (Fig. 6.6c').

Therefore when adding EDTA as an enhancement agent it is highly important to control sludge pH within the range of 2.5 - 7.7 to ensure optimum conditions for the removal of copper and iron from anaerobic granular sludge.

4.5. Practical application of the electrokinetics for sludge clean-up

The main difference in the both electrokinetic setups is the positioning of the electrodes. Thus, in the 'open' cell electrodes are inserted directly into the sludge and in the 'closed' cell electrodes are immersed into the electrolyte solution (Fig. 6.1). The more practical solution is to position electrodes straight to the contaminated medium or position them using different electrode wells or trenches. However, Alshawabkeh et. al. (1999) observed that this configuration may develop inactive electric fields between electrodes of the same polarity. Additionally, one of the reasons why copper and iron migration efficiency was higher in the 'open' cell could be that the electric field was non-uniform during the electrokinetic experiments

(Table 6.3a and c). Similar results were obtained by Turer and Genc (2005), where different electrokinetic units were tested for the Cu, Zn and Pb removal efficiency.

When electrodes are directly positioned into the sludge or any other contaminated medium, several questions arise, e.g. how to remove contaminants after the remediation process is over and how to prevent electrode from drying at the same time maintaining for example unsaturated conditions in the medium. Thus, Alshawabkeh et al. (1999) suggested that electrodes, used in electrokinetic experiments, should be chemically inert, electrically conductive and hollow. The hollow in the electrode can facilitate removal of contaminated solution via pumping. Also, hollow allows the injection of the purging solution into the subsurface if necessary.

Wieczorek et al. (2005) reported that in order to prevent electrode from drying, avoid the spreading of acid and base fronts and maintain unsaturated conditions in the medium it is necessary to employ a special electrode well system. For details please refer to Wieczorek et al. (2005).

The 'open' and 'closed' electrokinetic set-ups used in this study (Fig. 6.1) do not allow to calculating net removal efficiencies of copper and iron from the sludge cake. Hence, the accumulation and distribution efficiencies are presented as the major electrokinetic treatment assessment tool.

The highest accumulation values for copper and iron at a final pH of 7.7 and 2.5 in the sludge cake corresponded to the abundance of soluble and mobile species at these pH values(Table 6.3) as also observed by Kim et al. (2002), Velizarova et al. (2002) and Acar et al. (1993). The latter indicates that future optimization of the migration of charged contaminants out of sludge matrixes need to improve their solubility. Besides $EDTA^{4-}$ addition (Table 6.3), this could be also achieved by variations in temperature (Mohammadi et al., 2005), as increasing temperatures may fasten the transport of heavy metals towards the appropriate electrodes. Alternatively, the pH of the sludge cake could be reduced and therefore solubilization of contaminants could be achieved, by the addition of sulfur-oxidizing bacteria and subsequent aeration of the sludge cake, as these bacteria produce sulfuric acid from the reduced sulfur compounds present in anaerobic sludge (Maini et al., 2000).

5. Conclusions

Applied low-level electric current to anaerobic granular sludge in both 'open' and 'closed' cell layouts has significantly induced the mobility of contaminants towards electrodes.

The pH is an important factor in the mobility of copper under an externally applied electric field (40mA). At pH 12.5, there is no movement of copper ions in the sludge. At pH 2.5, copper and iron significantly move towards the cathode.

Surprisingly, the addition of EDTA at pH 2.5 failed to significantly induce the mobility of both copper and iron. However, it facilitated copper and iron migration towards the anode. This may be further used as an advantage in optimization of the overall electrokinetic process, for example to combine the consolidation of the sludge with removal of organic contaminants together with Me-EDTA. Moreover, during the consolidation, pore water moves exclusively towards the cathode and contaminants move towards the anode, where they can be extracted or removed using conventional physicochemical methods.

The 'open' cell layout yields higher copper and iron transport under the applied electric field than the 'closed' cell, therefore 'open' cell layout may be more efficiently applied *in situ*.

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CHAPTER 7: GENERAL DISCUSSION AND CONCLUSIONS

1. Summary

The present study aimed to investigate the main issues influencing efficient electrokinetic remediation of contaminated sand, timber waste and anaerobic granular sludge. Electrokinetic experiments were performed on artificially contaminated lake sand, CCA-treated timber waste and anaerobic granular sludge obtained from UASB reactor.

Focus was kept on optimum electrode number and spacing, electrokinetic cell layout, contaminant placement in the electrokinetic cell, pH, electric current, chelating agents, drainage and matrix aging on the basis of improving the contaminants desorption processes. Other points investigated were connected to the contaminant bonding in different waste media and the effect of bonding on the electrokinetic remediation process was investigated in details.

Valuable information was obtained due to the experiments preformed in this thesis, which facilitates the improvement of electrokinetic remediation technology at large. It was found (Chapter 3) that electrokinetic treatment, when only electromigration is taken into consideration, may be applied to the contaminated sand and it is an excellent alternative to conventional pump and treat technologies. There are several innovative aspects, which may assist in the development of the time and cost efficient electrokinetic remediation system *in situ*. Thus, the results obtained in Chapter 4 on the effect of different contaminated medium placement in the electrodialytic cell, may help to improve electrodialytic method, which can be further bettered for the applications of *in situ* treatment of not only CCA-treated timber waste but also contaminated soils and sludge.

Experiments with anaerobic granular sludge obtained from UASB reactors (Chapters 5 and 6) is another innovative aspect of this thesis. There were no earlier attempts demonstrated on the potential removal of heavy metals from this particular medium taking into the consideration different chemical heavy metal bonding to the sludge granules and its influence on the overall electrokinetic process efficiency.

First part of the thesis has been dedicated to the research and comprehension of electrokinetic phenomenon and chemical metal bonding in waste media. Acquired information served as a basis for developing a laboratory scale device, necessary for execution of laboratory scale experiments with contaminated sand and anaerobic granular sludge. In the final stage of the thesis, the electrokinetic cell was improved allowing for example to treat liquid media and adjust different flow rates. Therefore, the obtained expertise facilitated the development of a completely automated pilot scale electrokinetic cell, which will be used in further long duration electrokinetic experiments in soils and wastewater.

2. Theoretical considerations

Due to increased environmental pollution, there is a continuous search for the most efficient, sustainable and environmentally friendly contaminated media remediation technique. During the past decades, several new and innovative solutions for contaminant removal from soils, wastewater and sludge have been investigated and it is strongly believed that they will help to solve the environmental pollution. Despite numerous promising laboratory and pilot scale experiments, there are not many successfully implemented in situ remediation techniques yet. Because of uncertainty, lack of appropriate methodology and proven results many techniques are under way. It is likely that there will not be one single universal treatment technology. Instead, quite a large variety of technologies and their combinations suitable for different wastewater, soil and sludge remediation situations will be developed and implemented.

Although all successful and sustainable electrochemical technologies have not been completely investigated and implemented, there are several techniques which have attracted

increased interest among scientists and industry officials. Main advantages and disadvantages of the techniques are presented in Table 7.1. The information given in the table was collected and evaluated by the author of the thesis throughout the doctoral studies.

Table 7.1. Advantages and disadvantages of electroremediation techniques

Technique	Treated contaminants	Advantages	Disadvantages
Electrokinetics	Heavy metals, organics, radionuclides	- Favourable acidification of media (Cu, Zn, Pb, Ni cases) - Efficiency does not depend on ion concentration - Low cost and easy to implement	- Unfavourable acidification of the media (Cr, As cases) - Time consuming application - Solubility of contaminants and desorption from the contaminated matrix - Anomalies found in matrix (iron or iron oxides)
Electrosorbtion	Organic and inorganic contaminants	- Efficient entrapment of contaminant ions in the electrode polymer matrix - Eliminated pH jumps by pH-regulating chemicals in the electrode matrix	- Lack of proven results - Long time of implementation
Electrochemical ion exchange	Organic and inorganic contaminants	- Efficient capture of ion contaminants in porous castings and pumping out to the surface - Employment of ion exchanger to reduce post treatment contamination	- Cost inefficient procedure for cleaning effluents containing low levels of contaminants
Electrokinetic bioremediation	Organics, heavy metals, radionuclides	- No external microbial population needs to be supplied - Microorganisms can easily be directed to a specific location - Low cost and easy to implement	- Contaminant concentration may exceed microbial population toxic limits and microorganisms may die - Simultaneous remediation of contaminants may produce by-products toxic to microorganisms - Finding of the most efficient microorganisms - Biofilm coating difficulties onto the electrodes

Electrokinetic remediation is an innovative technology (as discussed in Chapters 1 - 6), which aims to remove heavy metals, organics and radionuclides from contaminated soil, sludge, wood and other contaminated media. It involves an application of a low level direct current (0.1 - 2.3 $mA.cm^{-2}$), which induces the movement of ionic species in the media-water solution towards the oppositely charged electrode (electromigration), a bulk flow of moisture present in the contaminated media from the anode to the cathode (electroosmosis) and a movement of charged particles or colloids in the applied electric field (electrophoresis).

For many years, the main emphasis of electrokinetic soil remediation was on saturated, fine-grained soils and clays, which led to the misconception that electrokinetics was not suitable for unsaturated, sandy soils. Laboratory scale experiments performed during the thesis for the first time proved that with appropriate technology and well-designed methods, it is possible to remediate heavy metals from sand also (Chapter 3).

The process may be enhanced by using ion exchange membranes to stop penetration of the unfavorable pH front into the contaminated medium (Kim et al., 2005). Indeed, in the

experiments without the usage of ion exchange membranes (Chapter 3 and Chapter 6), heavy metal migration efficiencies were poor in comparison to the one performed with ion exchange membranes. The process enhancement also may be achieved by addition of chemical reagents to increase contaminant removal rates (Wieczorek et al., 2005, Ottosen et al., 2005, Amrates et al., 2005). Certainly, the addition of oxalic acid assisted in the solubilization of copper and chromium from CCA-treated timber waste matrix (Chapter 4) but failed to demonstrate the desired effects in solubilization of heavy metals from anaerobic methanogenic sludge matrix (Chapters 5 and 6). Also, the efficiency of electrokinetic remediation may be increased by the application of ultrasound (Chung and Kamon, 2005) and other appropriate technological means such as combination of advanced oxidation and electrokinetic phenomenon (Park et al., 2005).

In order to efficiently exploit electrokinetic phenomenon for remediation of contaminated medias one needs to utilize multidisciplinary approach, i.e. profound knowledge of physical chemistry and electrochemistry, geotechnical engineering and transport modeling should be applied. The main drawbacks of the technique may be attributed to the lack of knowledge about the changes in heavy metal bonding to the different medias during the low level direct current treatment and heavy metal detachment not only from the surface but also from the inside of granules and particles. Therefore, the information obtained in Chapter 6 is of vital importance to the development of electrokinetic treatment technique. Importance of redox reactions should also be recognized.

3. Experimental design

For the practical application of electrokinetics, it is necessary to improve not only the efficiency of the remediation process itself, but also to decrease the remediation time, both of which will result in the reduction of the overall cost of the technique. 'Open' experimental set up used during the thesis was designed and tested as an essential part of the doctoral research. Despite the 'open' electrokinetic cell layout was considerably simple (Chapter 3 and Chapter 6), it allowed to determine the effects of electrical current, pH, electrode number and layout and complexing agents on the migration and speciation of selected heavy metals in contaminated medium. The remediation process efficiency was compared using the 'open' and 'closed' experimental setups during experiments with anaerobic granular sludge (Chapter 5 and 6). The advantage of the developed 'open' cell layout is that direct pH and other necessary parameters could be checked while the experiment is still running, allowing to consider the evolution of the electric field and pH gradients.

One very important factor in increasing the remediation efficiency as well as minimizing process costs and reducing time is to choose the most suitable electrodes, their number and spacing (as described in details in Chapter 3). Optimal electrode spacing and geometry help to achieve the highest remediation efficiencies because the inactive electric field is eliminated, contaminants move faster towards the appropriate electrode where they are subsequently removed (Alshawabkeh et al., 1999).

It has been found that an electric current density in the range of 1 – 10 A/m^2 has been the most efficient for the heavy metal removal from soils (Alshawabkeh, et al., 1999). Therefore, during laboratory scale experiments, the electric current density was kept in the range of 0.1 - 2.5 mA/cm^2 in the experiments with contaminated lake sand. Nevertheless, the most appropriate electric density and electric field depend on lots of factors to name the electrochemical properties of the matrix (electric conductivity in particular) and electrode geometry as well as distance between them among the few of them.

The electric field strength is known to be the most efficient in the range of 0.25 – 0.5 $V.cm^{-1}$ (Alshawabkeh et al., 1999) in the soils. The proposed optimum range was tested in three

matrices and it was found that the most efficient electric field was 0.8 $V.cm^{-1}$, thus the higher voltage input is required for the successful removal of heavy metals from lake sand and anaerobic granular sludge (as discussed in details in Chapters 3 and 5,6). However, experiments with CCA-treated timber waste proved that the optimum range proposed for soils also fits this particular matrix (Chapter 4).

4. Experimental results

Numerous laboratory scale experiments were performed to evaluate the feasibility of electrokinetic treatment techniques. In the experiments with sand and sludge, the matrices were artificially contaminated with 300 $mg.kg^{-1}$ and 1000 $mg.kg^{-1}$ of copper, respectively. However, CCA-treated timber waste was a real waste taken from out of service *Pinus pinaster* Ait Pole. The treated media was placed into the electrokinetic cells and subjected to the low level electricity treatment.

Determining the effect of electrode layout on the migration of copper in sand, the effect of complexing agents for the detachment of copper and chromium from CCA treated timber waste matrix, the effect of electric current, pH, complexing agents, electric cell layout and pre-incubation on copper and other selected heavy metal migration and speciation in anaerobic granular sludge, numerous experiments were performed.

4.1. Electrode layout, material and number

As stated in Chapter 3, electrokinetic cell layout, electrode material, number and spacing played an important role in achieving the successful and efficient removal of contaminants from the contaminated sand, which was taken as a sample porous medium.

Chemically inert and electrically conducting materials should be used as electrodes to prevent dissolution of electrodes and additional products introduction into the treated environment. During the doctoral research, silver and graphite electrodes were tested for the best efficiency (Chapter 3). The silver electrodes were consumed under the applied electric current, i.e. the anode in particular due to the acidic environment and by-products were introduced into the sand. Graphite electrodes presented efficient performance and were successfully used in later experiments for the heavy metal removal from contaminated sand. In addition, electrodes have to have a very good contact with the medium. Thus, in the performed experiments anodes were positioned directly into the sand.

According to performed experiments, factors affecting the selection of the electrode configuration were location and size of any inactive electric field spots, number and costs of electrodes per unit area to be treated and time requirements of the remediation process. In addition, the factors, which affected the selection of electrode spacing, were first of all costs and required treatment time.

During the performed study it was found that the two-anode system (linear or triangular) is the most efficient system for removing copper from contaminated lake sand (Chapter 3) when remediation of 91% was achieved. In addition, it is also important to take into consideration 2D and 3D electrode layouts. Hence, future experiments should be focused on obtaining the optimum electrode surface area, which is cost efficient, easy to implement and presents the highest removal efficiencies of contaminants from chosen media.

4.2. The effect of electric current

Laboratory scale experiments showed that electricity induces the movement of heavy metals during the electrokinetic treatment. Agreement of voltage fluctuation observed in

Chapters 3-6 with those cited in the literature (Ottosen et al. 2002; Velizarova et al. 2002) is very good. Therefore, the decrease in electric gradient is due to the H^+ front reaching the cathodic side, where is meets the OH^-. Formed acid assisted in the increased mobility of heavy metals with the exception of Cr species which favor alkaline environment, in the contaminated matrices.

4.3. The effect of complexing agents

Introduction of oxalic acid and EDTA to CCA-treated timber waste (Chapter 4) resulted in a change of the migration direction of copper and chromium in comparison to non-complexed metal behavior in the applied electric field.

It was observed that when the CCA-treated timber waste was placed with oxalic acid, oxalates or other compounds are formed (as discussed in details in Chapter 4). The predominant direction of those compounds was always found to be towards the anolyte solution indicating that negative species were the most predominant. The movement of copper towards the catholyte was negligible in all experiments with CCA- treated timber waste. However, the complete removal of copper and chromium was not achieved. One reason could be that the insoluble CuOx (copper oxalate) may prevail in the matrix. It is likely that insoluble compounds remained bound to the wooden chips matrix, and therefore impaired the overall migration process.

Chromium formed negative Cr (VI) complexes with oxalic acid and moved towards the anode during the electrokinetic treatment (Chapter 4). Hence, when the pH in the cathode compartment was significantly reduced (to the final pH of 2.5), chromium was also reduced to Cr (III) and moved towards the cathode as a positively charged complex or as Cr^{3+}.

4.4. pH evolution

As expected, the water electrolysis at the anode and cathode significantly influenced the pH in the samples (Chapters 3 - 6). At the anode, low pH area was developed due to the H^+ formation, while alkaline pH area was formed at the cathode due to the OH^- formation. However, the pH jump was not formed in the experiments with timbre waste, sand and anaerobic granular sludge when 'closed' electrokinetic cell was used. This was mainly due to the employment of ion exchange membrane which did not allow the penetration of OH^- ions into the treated medium and specific characteristics of treated media as discussed in details in Chapters 3 - 6.

4.5. The effect of electrokinetic treatment strategies on speciation and migration of copper and trace metals

The research showed that electrokinetic treatment at 0.8 $V.cm^{-1}$ for 14 days not only induced copper and trace metals mobility but also altered their fractionation in anaerobic granular sludge as described in details in Chapter 5. The latter was strongly influenced by the pH, sludge pre-incubation and the presence of EDTA. Copper showed extremely good affinity for the organic matter and sulfides present in the sludge (Chapter 5) which is in accordance to the numerous findings in the literature (Pattrick et al., 1997; Lu and Allen, 2002; Vulkan et al., 2002).

4.5.1. The effect of pH

Copper extracted was shown to increase in the organic / sulfides and residual fractions at the anode and cathode sides of the freshly copper amended sludge for a final pH of 7.7 and

surprisingly only at the anode side at final pH 4.2. This outlines the presence of negatively charged copper species.

4.5.2. The effect of sludge pre-incubation

The electrokinetic treatment of the pre-incubated copper amended sludges mainly influenced the metal accumulated in the organic / sulfides fraction, which was found to be relatively mobile in the electric field and accumulated in the anodic side of the electrokinetic cell.

When the sludge was pre-incubated with Cu for 30 days and then supplemented with EDTA before electrokinetic treatment, copper extracted in the residual and oxides fractions exclusively increased at the anode side at both pH conditions.

4.4.3. The effect of EDTA

Experiments proved that EDTA is efficient to decrease the copper content in the exchangeable / carbonates and oxides fractions of the fresh sludge, however no decrease was noticed in the organic sulfide and residual fractions, which may probably be attributed to the presence of sulfide precipitates which are efficient sorbents.

4.4.1. The behavior of trace metals in the sludge

The decrease in the residual fraction of trace elements compared the initial sample prior to electrokinetics treatment might be explained by the desorption of heavy metals from the sludge crystalline matrix (i.e., residual fraction) due to the application of electric current, which also induced a change in pH (Chapter 5). The removal of trace metals from the residual and organic / sulfides fractions were not efficient (Chapter 5) due to the presence of sulfides in anaerobic granular slduge.

The electrokinetic treatment at a final pH sludge of 7.7 increased calcium, iron and magnesium content in the exchangeable / carbonates fraction at the cathode side. In the same time, the macro elements accumulated in the oxides fraction decrease significantly in the three electrokinetic cell sections studied very likely due to a remobilization under the electric field and redistribution in other fractions such as the exchangeable / carbonates fraction or migration in the catholyte compartment as positive species. EDTA addition increases significantly the content of calcium, magnesium and iron in the organic /sulfides fraction at the cathode side compared to the non EDTA-treated sludge.

4.6. The effect of pH

4.6.1. The effect of pH on copper and iron migration in fresh anaerobic granular sludge

At low pH, copper tended to desorb from the sludge and entered into solution as positively charged ions (Chapter 5). The decrease in pH during the electrokinetic treatment consequently promoted the formation of soluble mobile copper compounds such as free Cu^{2+}, which caused copper accumulation at the cathode side of either the freshly amended and pre-incubated sludge.

The mobility of copper and iron in the electrokinetic cells and the efficiency of the electrokinetic movement of copper and iron in the sludge were low under the alkaline and slightly alkaline conditions compared to the migration of the contaminants at acidic pH (Chapter 6). This was most probably due to the formation of insoluble and hence immobile species such as

hydroxides and oxy-hydroxides, sulfides and carbonates. When the pH was adjusted to 2.5, copper as well as iron was significantly transported towards the cathode (see Chapter 6 for details).

4.6.2. Effect of pH on EDTA-supplemented anaerobic granular sludge

When the pH in the sludge was maintained at 12.5, EDTA addition did not induce the movement of either copper or iron species (Chapter 6), due to the formation of insoluble complexes. On the contrary, at the final pH of 7.7 in the sludge, copper migration towards the anode occurred, which can be attributed to the formation of $CuEDTA^{2-}$ or other negatively charged complexes. Also, at the pH 2.5, the migration of iron and copper to the anode suggested the transport of negatively charged species.

5. Practical considerations for the improved heavy metal electro-removal from contaminated matrices

Despite several innovative aspects of the technology were discovered during this thesis such as feasibility of treatment of contaminated sand with electrokinetic method and influence of the heavy metal fractionation on the efficiency of electrokinetic treatment, the particular emphasis in the future tests should also be put on the interaction of contaminants with the surface of waste media and profound comprehension on the distribution of contaminants between different fractions.

Despite the excellent research done by Acar et al (1993 and 1994), Acar and Alshawabkeh, (1993, 1996, 1997), Ribeiro et al (1997), Jakobsen et al (2004), Kim et al (2002) and other researchers, it is important to test, validate and evaluate additional methods to control the changes in chemical bonding of contaminants when the low level electric current in applied to the system. Also, the area around electrodes should be more developed, especially *in situ* regarding contaminants removal after the electrokinetic treatment.

To solubilise contaminants, besides EDTA addition this could be achieved by variations in temperature or addition of electron transfer mediators. Increased temperatures may fasten the transport of heavy metals towards the appropriate electrodes. However, the increased temperature may be applied to the system which favors desorption. Electron transport mediators such as anthraquinonic compounds AQDS, AQS (Bartlett et al., 1991) or even humic acids (Cervantes et al., 2002), may act similar to EDTA and thus may reduce the necessity for the addition of external chelating agents such as EDTA.

To determine the possible enhancement of the electrokinetic migration of heavy metals in contaminated sludge matrices, metal speciation techniques, as e.g. sequential extraction technique might be very beneficial. In addition to fractionation testing, further research is required using e.g. X-ray diffraction and Energy Dispersive X-ray Spectroscopy spectra with scanning/transmission electron photographs or X-ray absorption spectroscopy to develop a further understanding of changes in anaerobic granular sludges composition and morphology before and after electrokinetic treatment (Huang et al., 2003). A compilation of these results will provide a fundamental approach for geochemical modelling and assist in the development of effective electrokinetic remediation systems.

The present drawbacks of the electrokinetic technique might be overcome by coupling microbial metabolism (Jackman et al., 1999; Chillingar et al., 1997; deFlaun and Condee, 1997; Natarajan, 1992; Sale et al., 1967). This can be achieved by supplying e.g. elemental sulfur to acidify the soil by thiobacili (Natarajan, 1992). Alternatively, metal respiration can be optimized

by coating a biofilm on such microorganisms onto the electrodes, which allows utilizing heavy metal contaminants more efficient and removing the precipitated metals easier than in the electrokinetic cell layouts used in the current study. This is expected to reduce the remediation time, cost and energy consumption for the removal of heavy metals from contaminated media. This warrants further research to the utilization of microorganisms to enhance the efficiency of electrokinetic treatment, e.g. to reduce the heavy metal removal time.

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